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SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA

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DEVELOPMENT OF AN INFLATABLE
SELF-RIGIDIZING SPACE SHELTER AND SOLAR COLLECTOR
FROM HONEYCOMB SANDWICH MATERIAL

TECHNICAL DOCUMENTARY REPORT No. APL TDR 64-29

AIR FORCE AERO PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 8170, Task No. 817004
Project No. 3145, Task No. 314502

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200 - May 1964 - 162-38-766

FOREWORD

ABSTRACT

Properties which are obtainable by the curing of polymer systems by various applicable techniques were rapidly evaluated and a resin system for use in this concept of rigidization of expandable space structures was developed. An extensive search of the weaving industry revealed that no one can presently weave an actual honeycomb sandwich material that is completely flexible and has the faces woven as an integral part of the sandwich. Several fabrics which closely resembled a true honeycomb were used in the fabrication of the desired items.

The final items of the development program were a lightweight, expandable, self-rigidizing 5 ft. diameter solar collector and a lightweight, expandable self-rigidizing 7 ft. diameter by 7 ft. high cylindrical space shelter. Both final items were rigidized by vapor phase catalysis of a chemical rigidizing resin system. The study revealed that it is feasible and even desirable to design, fabricate, and rigidize flexible, self-rigidizing solar collectors and shelters for space application using a honeycomb type sandwich material as the basic structural material.

This report has been reviewed and is approved.

ROSS J. CALVERT, Chief
Support Techniques Branch
Technical Support Division

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SECTION 1

INTRODUCTION

The advent of manned space exploration has brought about an increased emphasis on strength-to-weight ratios and launch package volume. The time table of exploration calls for very large diameter solar collectors, space stations, and shelters to be transported into space. The transportation of these large size structures requires a technique of either assembling small modular components in space or the development of an expandable structure. It should be pointed out that these statements can also apply to limited war shelters and structures. Viron Division of Geophysics Corporation of America and Archer-Daniels-Midland Company, under AF Contract 33(657)-10409, are developing a technique which will not only satisfy the requirement of small package volume, but will also provide structures of very high strength-to-weight ratios. This initial effort has been directed toward producing terrestrial and aerospace shelters and space solar collectors.

The structural concept utilizes a woven fibrous corrugated or honeycomb type core which is impregnated with a plastic resin system. This resin-honeycomb combination is initially flexible, but on command will rigidize into a rigid fiber-plastic composite. The exterior surface skins and interior cell walls or corrugation webs are impregnated with the subject resin system. Rigidization of the resin system can occur from radiation cross linking, plasticizer boil off, or vapor phase catalysis. The latter two have been found to be the most suitable under this research effort. This structure when rigidized will produce results comparable to the well known rigid honeycomb structures. This overall concept was originated by Sydney Allinikov and Fred Forbes of the Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

SECTION 2

OBJECTIVES

The objectives of this study were to show feasibility of the design, fabrication, and chemical rigidization of structures for space application using a completely flexible sandwich type material as the basic construction material. The material was then to be impregnated with a plastic resin system which, on command, would rigidize into a rigid fiber-plastic composite.

Specific objectives were to show the feasibility for two items; 1) a space shelter, and 2) a solar energy concentrator.

1. The space shelter was to be a 7 ft. diameter by 5 ft. high cylinder with a hemispherical dome top and a flat floor. The structure was to be capable of withstanding an internal pressure of 0 to 14 psi in essentially a complete vacuum and withstand a uniform loading of 100 psi over the roof surface.

2. The 5 ft. diameter solar energy concentrator, using sandwich type structural material for structural rigidity, was to weigh about 0.2 lb./ft^2 of reflective surface area, have a reflectivity of 0.87 to the solar spectrum, and be within $\pm$ 1/4° of a paraboloid over 98% of the surface.

SECTION 3

LITERATURE SURVEY

A. General

This study was undertaken to show feasibility of design and fabrication of an inflatable self-rigidizing aerospace shelter and solar collector using honeycomb sandwich type structural material. Since the space environment imposes more stringent requirements on the behavior of materials, a materials requirement survey is a large part of this feasibility demonstration.

B. Materials Requirement Survey

A major portion of the materials which will be used in this project will very likely be of organic origin. This becomes apparent when note is made of densities encountered in organic polymeric products and the high strength-to-weight ratios possible in laminate forms. Plastics have lower densities than most metals, often as low as 1/6 or 1/7 that of steel and about 1/2 that of magnesium (Ref. 1).

In selecting materials suitable for use in a space environment it is necessary to determine in advance what effect such an environment will have on the engineering properties of the materials under consideration. Since this project is primarily concerned with organic polymers, the factors influencing their degradation are of major interest. A brief survey of the literature shows that much experimental work has been done and is currently being conducted in an attempt to discover optimum materials for use in space.

Major factors of the space environment which will affect the performance of materials are:

1. High vacuum
2. Ultra Violet Radiation
3. Meteoroid bombardment
4. Thermal gradients
5. Temperature Cycling
6. High energy radiation

1. High Vacuum

Of the many hazards to space materials, one of the greatest is the effect of high vacuum. Fortunately, considerable data has been accumulated in this area. None is actual experimental data at the hard vacuum experienced in a space environment, but the simulation has been well carried out. A satisfactory simulation of space vacuum for laboratory studies of sublimation and decomposition effects on a material can be obtained by reducing the pressure to a point where the mean free path of escaping molecules is large enough that the molecule will strike the wall. Cooled walls will then prevent any resublimation from the wall deposits. Normally 10^{-5} mm Hg will give mean free paths of about 6 feet, and will be sufficiently low.

Langmuir presented an equation in 1913 which predicts the rate at which molecules leave a surface into vacuum:

$$W = \frac{P}{17.14} \left(\frac{M}{T}\right)^{\frac{1}{2}}$$

where:

W = rate of sublimation or evaporation, gm/cm^2 - sec.
P = vapor pressure of the material, mm Hg.
M = molecular weight of the material in the gas phase
T = temperature, $^{\circ}K$
This can also be expressed as:
$$S = 1.85 \times 10^6 \ (p//\rho) \left(\frac{M}{T}\right)^{\frac{1}{2}}$$

where:

S = sublimation rate, cm/yr
ρ = density of the solid material, gm/cm^3

These equations apply when no escaping molecules can return to the surface of interest and resublime. Therefore, if the vapor pressures and molecular weights are well known, the rate of sublimation can be confidently determined from either of the above equations.

The effect of high vacuum on organic materials is to break the long chains into smaller, more volatile fragments (Ref. 2). Therefore, calculations based on vapor or decomposition pressures are not usually useful for the organic material of interest, and it is necessary to experimentally determine the weight loss of polymers in space.

G. F. Matacek, WADC, Wright-Patterson Air Force Base, (Ref. 3) reported that, out of 13 different organic polymers held in a vacuum of 1×10^{-5}mm Hg for 24 hours, no weight losses occurred. When these samples were subjected to heat, the weight losses of most materials became significant. Table 1 shows the weight losses of materials after 24 hours at given temperatures (Ref. 3).

Formulation 13 shows that a barrier coating of silicone polymer reduced the volatilization of a less stable silicone alkyd by more than 50%. This indicates that a coating material might not only serve to prevent or retard the degradation of the underlying material, but might also act to prevent the volatile fragments, if any, from escaping and possibly enabling them to re-combine. Table 1 shows that the materials least affected by low vacuum and temperatures up to 500°F for 24 hours were styrene butadiene, phenolic and chlorotrifluoroethylene fluoride.

Jaffe and Rittenhouse (Ref. 2) state that a 1 or 2% weight loss is not detrimental to engineering properties of plastics. Materials experiencing over 10% weight loss should be avoided as this amount of loss produces drastic reduction in physical properties. Surface materials containing plasticizers should be avoided as weight losses of less than 10% can cause brittleness, crazing, and a loss of adhesion to the substrate.

	24 Hours Exposure	% Weight Loss			
Formulation and Chemical Type	Ambient Temperature	200°F	300°F	400°F	500°F
Alkyd	0.0	4.1	9.8	17.1	25.3
Silicone-Alkyd	0.0	4.4	10.9	26.2	50.2
Linseed Oil	0.0	3.3	10.5	17.5	31.1
Acrylic	0.0	8.2	17.5	19.1	47.6
Styrene-Butadiene	0.0	1.4	2.7	4.3	9.6
Polyvinyl-Butyral	0.0	0.5	8.7	46.8	70.3
Phenolic	0.0	0.8	4.5	6.1	6.1
Kel-F	0.1	0.3	1.6	2.7	2.7
Cell. Acet. Butyrate	0.0	0.1	2.3	4.1	31.5
Nitrocellulose	0.0	0.7	47.2	73.6	80.8
Polysulfide	0.0	11.7	63.1	64.0	64.6
Silicone-Alkyd (film)	0.0	2.7	11.3	24.8	39.6
Silicone Coated Silicone-Alkyd (film)	0.0	0.5	2.3	8.5	17.0

TABLE 1. WEIGHT LOSS FOR VARIOUS ORGANIC POLYMERS WITH TIME AND TEMPERATURE AT 10^{-5} mm Hg

Vapor pressures of high molecular weight plastic are thought to be low enough so that at moderate temperatures the material will not volatilize and degrade. In a referenced article by R. E. Mauri (Ref. 4), vapor pressures of several organic materials are given as in Table 2. Jaffe and Rittenhouse (Ref. 2), have compiled an excellent table showing the temperatures for a 10% weight loss per year in a vacuum.

2. Ultraviolet

Solar radiation studies are conducted by using commercially available lamps which produce ultraviolet wave lengths from about 2000 A^o to 7500 A^o. The major portion of the solar spectrum producing molecular excitement is in the region between 2800 and 3800 A^o units.

The effect of ultraviolet energy on polymeric films at the earths surface has been widely studied by paint, pigment, and plastic manufacturers for many years. Since a large portion of the solar spectrum is "filtered" out by the earth's atmosphere, little information is available on the effects of the total solar spectrum on material. In general it is known that solar energy incident to an organic polymeric surface will cause changes in the molecular structure with resulting polymeric rearrangement or degradation.

In an oxygen bearing atmosphere degradation by ultraviolet is thought to be the result of free radical formation which may induce (1) the breaking off of smaller chain fragments which may volatilize and (2) the cross linking of the remaining chain segments. Cross linking of the larger chain fragments may, however, form larger molecules and actually up-grade some strength properties but beyond a certain point the polymer will become brittle causing crazing or cracking. Work done at the Naval Research Lab, Washington, D. C. (Ref. 5) demonstrated that the degradation of polymers will take place less rapidly in vacuum than in air. In this work, experiments also indicated that the portion of the ultraviolet spectrum between about 1100 A^o and 2000 A^o has a much lesser quantitative effect on polymeric materials than the portion between 2000 and 4000 A^o. This is probably explained by the lower total intensity of the shorter wave length portion.

Wahl and Lapp of Cornell Aeronautical Lab., Inc., (Ref. 6) studied effects of low vacuum and ultraviolet radiation wave lengths, ranging from 2500-5800 A^o with an energy flux equivalent to 2 pyrons*, on three types of material in glass laminate form. These materials were unsaturated polyester, epoxy, and phenolic resins. They found that after 500 hours of exposure, the polyester laminate lost 0.789% in weight, increased in flexural strength from 72,000 to 74,000 psi and increased in compressive strength from 43,000 to 49,000 psi. Similar results were obtained with epoxy and phenolic resin laminates. The authors concluded that unless exposed to other unknown factors or high temperatures these materials would probably be useful in space environment. When the ultraviolet intensity

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* A Pyron is 1 cal/cm^2/min.

Material	Vapor Pressure at 25°C, mm Hg.
Mylar	1×10^{-7}
Saran	3×10^{-8}
Vinyl	1×10^{-8}
Teflon	1×10^{-7}
Nylon	1×10^{-9}
Hycar Rubber (Buna-N)	4×10^{-5}
Butyl Rubber	1×10^{-5}
Polyethylene	2×10^{-8}

TABLE 2.   VAPOR PRESSURES OF VARIOUS ORGANIC POLYMERS

was increased to 4.9 pyrons in vacuum, all three types lost considerable flexural strength after just 3 hours. The temperature of the samples reached a maximum of 465°F, the phenolic laminates showed the greatest weight loss but retained a larger percentage, 85%, of its original flexural strength. Another part of this work indicated that no significant dimensional change or weight loss occurred on samples of teflon when subjected to an environment of low vacuum and ultraviolet radiation of about 2 pyrons for a period of 96 hours.

Scientists at DuPont (Ref. 7) report that a film of Tedlar after nearly 20 years of exposure shows remarkable retention of properties. Recent work by R. G. Schmitt and R. C. Hirt (Ref. 8) has shown that changes induced by ultraviolet radiation in many types of polymeric coatings can be reduced by a factor of 30 to 5000 thru the use of certain benzoyl substituted ferrocent compounds used as ultraviolet absorbers.

3. Meteoroid Bombardment

The damage to surfaces from high speed meteoroids and micrometeorites is probably not as great a hazard as formerly thought. A. H. Landrock (Ref. 9) in a summary of other work states that the extent of micrometeorite damage is similar to some of the milder radiation effects.

Studies at Ames Research Center of NASA (Ref. 10) have indicated the particles scattered from the lunar surface may be hazardous to personnel as well as to materials. The article stated that the particles are scattered when a high velocity meteoroid strikes the dust and rubble of the lunar surface. About 1/2 of the kinetic energy of the meteoroid is thought to be transferred to the scattered particles.

4. Space Temperatures

The equilibrium temperature of simple geometric shaped bodies in a space environment can be determined to within small error by coupling empirical results with theoretical analysis.

The equilibrium temperature that a body assumes is dependent on three factors:

a. The geometrical shape of the body.

b. The emissive, absorbtive, and conductive characteristics of the material of which the body is composed.

c. The position of the body in space relative to incoming solar radiation, earth albedo radiation, and earth black body radiation.

Equilibrium temperature calculations on complex geometrical shapes are accomplished by reducing the shape to a collection of simple geometric shapes such as flat plates and cylindrical or spherical surfaces. Analysis of such surfaces are straight forward and correct within several percent error.

The radiation characteristics of the materials of which the body is composed can be determined empirically. The empirical data needed is:

α_s = absorbtion of 6000° K solar radiation

α_s = absorbtion of 6000° K earth albedo radiation

α_e = absorbtion of 300° K earth black body radiation

ϵ_s = emissivity of 6000° K solar radiation

ϵ_a = emissivity of 6000° K earth albedo radiation

ϵ_e = emissivity of 300° K earth black body radiation

Values of these parameters are on file at VIRON for most film material in inflatable devices.

The position of the body in space relative to the earth and sun introduces form factors in the following general equation for determining the body equilibrium temperature.

Energy absorbed = energy emitted (at equilibrium)

Energy absorbed = $\sigma \alpha_s T_s^4 + \sigma \alpha_a T_a^4 \, \sigma \alpha_e T_e^4$

where $\qquad \sigma$ = Boltzman constant

$\qquad$ T = the absolute temperature of incoming radiation.

Energy emitted = $\sigma \epsilon T^4$

where $\qquad \epsilon$ = the body emissivity at the body temperature (determined by a reiteration process from ϵ_s, ϵ_a, ϵ_e,

$\qquad$ T = the equilibrium temperature of the body.

So, $\quad \sigma \epsilon T^4 = \sigma \alpha_s T_s^4 + \sigma \alpha_a T_a^4 + \sigma \alpha_e T_e^4$.

After introducing the correct form factors due to the space position of the body, the equilibrium temperature of the body can be accurately determined.

C. Honeycomb

Honeycomb sandwich material generally consists of an array of cells bonded perpendicularly between two faces. A large variety of materials such as glass or other fabrics, aluminum, plastics, and paper can be made into the core material. The present state of the art however, seems to require that the core material be in a semi-rigid state prior to fabrication if the cost is to be kept reasonable.

Virtually any bondable material can be used for honeycomb facings. Desirable qualities are high tensile and compressive strength-to-weight ratios. Most commonly used facing materials are aluminum, steel, wood, and glass reinforced plastics. Honeycomb sandwich construction offers a very high strength-to-weight ratio, resi nce to heat transfer and vibration, flexibility of strength designs by changing cell size, etc., and a double wall which is desirable in pressure vessels.

1. Theory of Sandwich Construction

Honeycomb structures are very similar to I beams. The facings correspond to the flanges and the cell structure corresponds to the web. The advantage is that a high strength material can be placed far from the neutral axis to increase the section modulus. The facings can act as a single unit since the cell structure provides a continuous support for the facings allowing loads even beyond the yield strength of the facings without crimping or buckling. The adhesive which bonds the honeycomb to the facings must sustain full shear loads to retain the effectiveness of the honeycomb sandwich as an integral unit.

The assumptions are made in honeycomb structures theory that if the structure is loaded as a beam the honeycomb core resists shear loads and the facings resist the bending force moments. Similarly, if the structure is loaded as a column, the facings resist the column forces and the core acts only as a stablizer to prevent crimping or buckling (Ref. 11).

2. Honeycomb Structures Calculations

The stresses present in a honeycomb panel can be calculated from the same equations used for I beam calculations. Ref. 12-14 give a complete description of the methods used in the design of honeycomb structures. Ref. 12 is a very complete coverage of sandwich panel design, including extensive theoretical and empirical results for many different types of applications.

SECTION 4

RESIN SYSTEM RESEARCH

A. Background

The initial effort of this research dealt with the rapid screening of available resin systems to determine which should be further investigated. The substrate material used for evaluation of the resins was primarily glass because of its availability and desirable characteristics in reinforced plastic systems. A regenerated cellulose acetate (Fortisan) obtained from Celanese Corporation of America was also evaluated and demonstrated excellent compatibility with the systems chosen for evaluation. From this initial work it is concluded that Fortisan should be carefully evaluated as a possible core material for honeycomb construction. Zein fiber, wool, and cellulosics were also screened but were dropped because of unavailability or inadequate physical strengths.

B. Rigidizing Systems

Three methods of rigidizing resin impregnated structures were con̄ ̄dered:

1. Vapor phase catalysis

2. Plasticizer boil off

3. Radiation catalysis

Each of the above methods has certain advantages and disadvantages. Each one will be discussed in detail with our conclusions based on experimental screening and evaluation.

1. Vapor Phase Rigidification

The major emphasis of this investigation was conducted on vapor phase curing systems. A rapid screening of the physical properties observed from commercially available resin systems and convenient catalyst systems was undertaken. These included the following:

Resin System	Catalyst
a. Urethanes	Water, amine
b. Epoxy	Amines, Lewis acids
c. Furfural resins	Acidic catalyst
d. Phenyl silanes	Water, amines
e. Polyester	Volatile peroxide (t butylperoxy isopropyl carbonate PPG)

The concept of curing a resin system with the vapor of catalysts is a new research area of high interest. It is of importance to note that in vapor catalyst systems, a relatively small amount of molecular vapor is available at any one time, consequently the ability to obtain a complete degree of cross-linking is of the foremost importance. A resin system, with functional groups which react with a catalyst at moderate temperatures and subsequently obtains a high degree of crosslinking, is needed.

a. Urethanes

The objectives of this program, as outlined in the introduction, call for a resin system that can be a flexible impregnant of a structural substrate, packageable, and upon command in space, deploy itself by self-expansion and rigidify with sufficient physical strengths through one of the three mechanisms discussed previously. The polyurethanes fulfill such requirements. Polyurethane resin intermediates were selected for complete evaluation as rigidizing agents for expandable aerospace structures because of their reactivity at modest temperature with compounds containing active hydrogens. We have demonstrated that urethane coatings applied as thin films will provide reinforced glass plastic systems which will meet the strength requirements.

A polyurethane polymer has a repeating number of urethane or urea func-tional groups along with aliphatic and/or aromatic hydrocarbons, ester, ether and amide groups. Ordinarily a urethane prepolymer can best be formed by reacting polyfunctional hydroxyl compounds, e.g., hydroxyl terminated isocyanates. A structure of a typical linear polyurethane derived from a dihydroxy compound can be illustrated by the following equation:

$$HOROH + OCNR'NCO \longrightarrow \left[RO\text{-}\overset{O}{\overset{\|}{C}}NHR' - NH\overset{O}{\overset{\|}{C}}\text{-}O\right]_n.$$
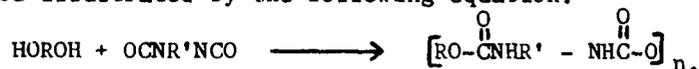
However, a one component urethane prepolymer depends upon water vapor for curing according to the following equation:

$$R\text{-}NCO + H_2O \longrightarrow R\text{-}NH_2 + CO_2$$

$$RNH_2 + RNCO \longrightarrow RNHCONHR.$$
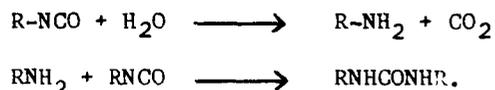
The effort of this program was devoted to the screening of candidate urethane prepolymers for use as impregnants of honeycomb glass fabrics. The reader is referred to progress reports submitted by Wyandotte Chemicals Corporation under Contract AF 33(657)-9174 for results of independent efforts on urethane systems.

The research effort was devoted to (1) Characterization of urethane prepolymers including composition, cure time under vacuum conditions with catalysts, and visual properties of moisture cured laminates, (2) Physical data-gathering of urethane free films and urethane impregnated laminates, and (3) Catalyst study involving resin impregnated structures under space and terrestrial environment.

1. Characterization of Urethane Prepolymers

The prepolymers evaluated as impregnants are described in Table 3. The basic compositions of the polymers involved a short diol, triol, and a poly-propylene glycol of medium molecular weight and a diisocyanate. The prepolymers were formulated at 50% non-volatile content to enable convenient methods of application. In the absence of moisture, shelf lives of 18 months have been observed. The free isocyanate content of these prepolymers range from 4 to 6% based on 50% solids. By varying the relative amounts of short-chain diols in the formulation, or by modifying the molecular weights of either the short-chain or long-chain diol, virtually any degree of hardness can be achieved.

The cure time requirements and visual property inspection of moisture cured laminates are outlined in Table 4. The structural fabrics used in these evaluations were Fortisan fabric style NW 372 and glass satin weave style 181.

2. Physical Data-Gathering

Unreinforced film physical data of the prepolymers are recorded in Table 5. These samples were prepared at 10 mil thickness and cured at $75^{\circ}F$ and 50% humidity. The physical properties of these films were determined after two weeks of curing.

Table 6 records the tensile and flexural properties of 1 and 3 ply laminates prepared from 181 glass fabric impregnated with urethane pre-polymer and cured at 50% relative humidity at $75^{\circ}F$ for three days. The flexural properties of the laminates were determined according to ASTM D-790.

3. Catalyst-Resin System Relationship

The following parameters affect the overall performance of the urethane:

a. Solvation of the urethane prepolymer

b. Resin-glass weight ratio

c. Cure rate variations

d. Methods of catalyst deployment

Solvation of the Urethane Prepolymer

The urethane prepolymers described in this report are isocyanate terminated polymers prepared by the reaction of diisocyanates with polyols (Table 3). The ratio of diisocyanate to polyol is selected so that a soluble urethane polymer of molecular weight between 1500 and 3000 which possesses terminal isocyanate groups is formed. Upon application, such a polymer may then react with moisture

Sample Designation	1000 MW Diol	400 MW Diol	700 MW Diol	1,3-Butylene Glycol	Other Glycol	TMP	400 MW Triol	TDI	Other Diisocyanate
972001		1.4		.6		2			(MDI) 8
972002		1.2		.8		2			(MDI) 8
972003		1		1		2		8	
452301			1			1.5		5.85	
452403	1		1			2		8	
8158-5-2		.8		1.2		2		8	
8158-5-10		1			(Dowenol 122) 1	2		8	
8158-5-19		1		1		2		6	TODI (2)
8158-5-15		1			(Propylene glycol) 1	2		8	
8158-5-7		1			(HBPA) 1	2		8	

TABLE 3. MOLAR COMPOSITION OF URETHANE PREPOLYMERS

Sample #	Resin % NCO Based on 50% solids	Cure Time Pressure	Results
452301	4.5% NCO 20% PVC	48 hours .25 mm Hg	H_2O cured rigid sample
452302	452301 + 4.5% NCO 20% PVC	48 hours .25 mm Hg	Propylene diamine cure less rigid than sample #452301
452402	20% weight 452403 +SMA resin 1000A	48 hours 0.25 mm Hg	H_2O cure excellent rigidity
452403 Fortisan NW 372	4.5-5% NCO	24 hours 0.1 mm Hg	H_2O cure, good rigidity tensile strength doubled over untreated Fortisan NW 372
453001 Fortisan NW 372	20% PVC + 452302	8 hours 0.25 mm Hg	Fair rigidity with H_2O cure
		24 hours	Good rigidity
453002 Fortisan NW 372	452402 + 2% by weight DML	8 hours 0.25 mm	Good rigidity
453021 Fortisan NW 372	ADM EP 8150 20% NCO	12 hours .005 mm	Rubbery
453202 Fortisan NW 372	ADM EP 8215 10% NCO	12 hours .005 mm	Semi-rigid
453203 Fortisan NW 372	ADM EP 8215 5% dimethyl lauryl amine	12 hours .005 mm	Semi-rigid
453204 Fortisan NW 372	ADM EP 7715 10% NCO	12 hours .005 mm	Non-rigid
453801 Fortisan NW 372	4.5-5% NCO Same as 452301	12 hours .005 mm	Good rigidity
453803 Glass cloth 181	Same as 453801	12 hours 0.05 mm Hg	Good rigidity

TABLE 4. VISUAL PROPERTIES OF MOISTURE CURED LAMINATES

Sample #	Resin % NCO Based on 50% solids	Cure Time Pressure	Results
453804 Glass cloth 181	Same as 453803	12 hours 0.05 mm Hg Propylene diamine	Rubbery
453805 Fortisan NW 372	%NCO 4.5-5% Same as 452403	48 hours Atmospheric pressure H_2O vapor, final cure 2 hours 0.005 mm Hg	Excellent rigidity
453806 Glass cloth 181	% NCO 4.5-5% Same as 452403	48 hours atmospheric pressure H_2O vapor, final cure 2 hours 0.005 mm Hg	Excellent rigidity
453807 Glass 181	% NCO 4.5-5% Same as 452403	48 hours Atmospheric pressure H_2O vapor, final cure 2 hours 0.005 mm Hg	Excellent rigidity
454601 Glass cloth 181	Tranco 560B 5% NCO	24 hours/H_2O 0.05 mm Hg	Flexible
454602 Fortisan NW 372	Tranco 560B 5% NCO	24 hours H_2O 0.05 mm Hg	Semi-rigid
454603 Glass Cloth 181	Tranco 560A 5% NCO	24 hours H_2O 0.05 mm Hg	Semi-rigid
454901 Glass Cloth 181	5-6% NCO	H_2O 48 hours 0.05 mm Hg	Good rigidity
454902 Fortisan NW 372	5-6% NCO	H_2O 48 hours 0.05 mm Hg	Good rigidity

TABLE 4.   VISUAL PROPERTIES OF MOISTURE CURED LAMINATES CONTINUED.

Sample #	Resin % NCO Based on 50% solids	Cure Time Pressure	Results
454903 Glass Cloth		H_2O 48 hours 0.05 mm Hg	Good rigidity
454904 Fortisan NW 372		H_2O, 48 hours 0.05 mm Hg	Good rigidity
455101 Glass Cloth Style 181	Weight/20% PVC	48 hours, H_2O 0.25 mm Hg	Good rigidity
972002 Glass Cloth 181	4.5%	48 hours 50% humidity 75°F	Good rigidity
972002 Glass 181	4-5%	48 hours 50% humidity 75°F	Good rigidity
972003	5%	48 hours 50% humidity 75°F	Good rigidity
972003 Glass 181	10% SMA Resin	48 hours 50% humidity	Good rigidity
972003 Glass 181	10%. Geon 121	48 hours 50% RH	Good rigidity

TABLE 4. VISUAL PROPERTIES OF MOISTURE CURED LAMINATES CONTINUED.

Sample #	Tensile PSI	% Elong
452403	8,696	5
453801	7,260	5.5
453002	7,060	6.0
972001	9,030	17.4
972003	10,800	6
8158-5-2	10,800	5.6
8158-5-3	11,800	6.0
8158-5-7	11,400	5.0
8158-5-10	11,900	9.0
8158-5-15	10,300	5.9
8158-5-19	9,680	3.44
8158-5-24	8,760	13.8

TABLE 5. TENSILE PROPERTIES OF UNREINFORCED FILMS

OF MOISTURE CURED URETHANE PREPOLYMERS

Sample[1]	Tensile psi	Flex psi	Modulus of Elasticity 10^{-6} psi	Yield Load lbs.	Thickness inches
452403	25,765				
453001	16,353				
453002	23,646				
453806	17,800				
454601	13,355				
454602	17,530				
455101	25,060				
*972001	19,722	10,700	.64	7.60	0.046
*972002	17,763	12,300	1.3	5.60	0.037
*972003	24,473	9,500	.89	2.90	0.030
**972003	21,200	7,000			
***972003	21,300				

[1]All physical constants were determined on a standard Instron tester.

*Flex strengths run on 3 ply laminates

**10% by weight SMA Resin

***10% by weight PVC

TABLE 6. PHYSICAL PROPERTIES OF URETHANE PREPOLYMER AND GLASS LAMINATES

to form a high molecular weight polymer coating. The vehicle described is
most conveniently made at 50% non-volatile material content. The viscosity
of this vehicle at room temperature (700 $\pm$ 75 Brookfield, cps) is suitable
for conventional methods of application. Saturation of glass weave fabrics
(Raypan or Wimpfheimer aerospace structures' is easily accomplished thru hand
lay-up, spray gun technique, or vacuum impregnation. The volatile component
of these vehicles is a solvent system mixture of xylene-cellulose acetate or
toluene/butyl acetate.

Resin-Glass Weight Ratio

The weight ratio of resin to glass has a direct relationship to the
ultimate strength to weight performance of the rigidized structure. In
addition to the weight consideration, cure time and ultimate strength are
affected by the percent of resin used. The less resin used for impregnation,
the shorter the cure time and the higher the degree of cure which is obtained.
This is apparently from the consideration that vapor catalysis of a condensation
polymerization is dependent on penetration into the resin mass. Conversely,
any less resin than that required to saturate the glass results in lower than
maximum strengths. This information concerning the minimum resin necessary
for maximum strength was desired.

In order to determine the minimum resin concentration required, the
weight ratio of resin to glass was varied in a series of experiments. Results
indicated that 20% resin solids is sufficient to achieve rigidization, but not
maximum strength. The larger honeycomb glass fabric structures have required
a resin content of between 30 to 40% resin for highest strength-to-weight ratios.

Cure Rate Variations

Variations in the cure rate were observed as a consequence of the volatile
solvent used with the urethane prepolymers. A series of experiments were
conducted on resin impregnated structures with and without prior removal of the
volatile solvent. In both instances the structures were subsequently cured
with water vapor at reduced pressures (5×10^{-2} mm/Hg). Removal of solvent
before water vapor contact reduced the cure time by a factor of two. Complete
solvent removal from the impregnated structures was accomplished by placing them
in a 12" desiccator and evacuating (5×10^{-2} mm/Hg) for 18 hours. Before open-
ing the desiccator to the atmosphere, nitrogen was bled in to provide an inert
blanket in order to exclude atmospheric moisture as much as possible. Upon
examination the structure was completely flexible and essentially tack free.
After compression of the structure it was placed in a vacuum chamber and connected
by means of tubing to a water supply. Evacuation of the system (5×10^{-2} mm/Hg)
caused volatilization of the water with the result that the structure fully
expanded and rigidified in the 4 hour time period. A most noteworthy improvement
in cure time was observed when a 90 - 10% weight ratio of water to triethyl amine
co-catalyst system was employed. This catalyst system yielded approximately one
hour cure times for resin impregnated glass structures at room temperature
conditions. Investigation of this reactive catalyst system with and without
prior removal of solvent from resin impregnated structures indicated solvent

Sample[1]	Tensile psi	Flex psi	Modulus of Elasticity 10^{-6} psi	Yield Load lbs.	Thickness inches
452403	25,765				
453001	16,353				
453002	23,646				
453806	17,800				
454601	13,355				
454602	17,530				
455101	25,060				
*972001	19,722	10,700	.64	7.60	0.046
*972002	17,763	12,300	1.3	5.60	0.037
*972003	24,473	9,500	.89	2.90	0.030
**972003	21,200	7,000			
***972003	21,300				

[1]All physical constants were determined on a standard Instron tester.

*Flex strengths run on 3 ply laminates

**10% by weight SMA Resin

***10% by weight PVC

TABLE 6. PHYSICAL PROPERTIES OF URETHANE PREPOLYMER AND GLASS LAMINATES

removal is not a critical parameter when employing water-triethylamine as co-catalyst, since cure rates were identical. The triethylamine greatly activates the isocyanate functional group by complex formation and renders the irocyanate more susceptible to attack by the water molecule. This can be illustrated by the following equation:

$$R'NCO + R_3N \rightleftharpoons \left[\begin{array}{c} R'N = C-O \\ \nearrow \\ R \diagdown \underset{R}{\overset{N}{|}} \diagup R \end{array} \right] \xrightarrow{HOH} \left[R'NHCOOH \right] + R_3N$$

$$k_1 \qquad \downarrow \; -CO_2$$

$$R'NH_2$$

$$R'NH_2 + R'NCO \xrightarrow{\qquad k_2 \qquad} R'NHCONHR'$$
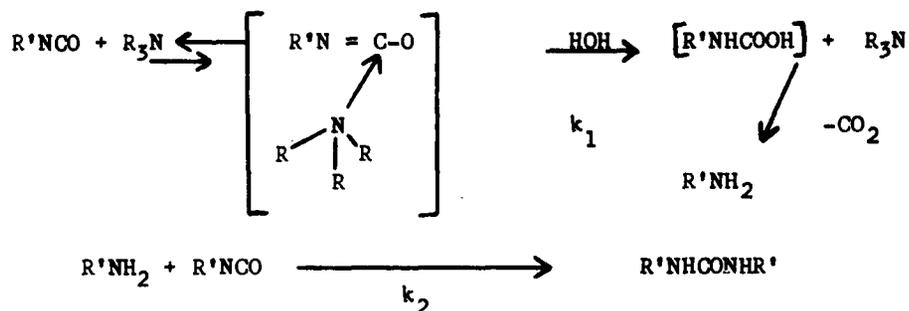
In essence, what the addition of triethylamine accomplishes is to speed up the reaction of the isocyanate with water, k_1. The unstable carbamic acid loses carbon dioxide and forms the primary amine group which reacts rapidly with another isocyanate, k_2, to form the crosslinked disubstituted urea.

In this sequence, k_2 is still greater than k_1, which is necessary for effective crosslinking; however the overall reactivity of k_1 is greatly enhanced when compared to an uncatalyzed water-isocyanate reaction. This factor is also evident under vapor catalyst conditions as the experimental results described above indicate. Apparently the catalytic effect of the triethylamine is sufficient to nullify the cure rate increase observed by prior removal of solvent.

Methods of Catalyst Deployment

Several mechanical devices, geared to self-contain catalyst within the resin system and to release it upon command in the environment desired, have been explored. One of these involves the use of polyethylene tubules which can be inserted between the flutes of three-dimensional integrally woven fluted core material (Raypan) and subsequently filled with catalyst. The ends when sealed give a catalyst container within the system. Such a system has shown limited operational success.

A second method that shows initial feasibility involves coating solid hydrates with a thin resin layer. Upon desiccation these materials give up about 33% of their chemically held water after three ho rs at .1 mm/Hg of pressure.

A third method involves coating a solid lightweight absorbing material, such as vermiculite, with a thin resin coating. This material is capable of absorbing up to 80% of its weight with water. Under vacuum environment as high as 50% of the retained water can be extracted.

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These methods of water containment are highly efficient and add little weight to the system. The materials are coated with a thin coating of Admiral 351 which is a cyclopentadiene copolymer resin.

4. Discussion of Results

The structure/property relationship in urethane polymers is dependent on many factors. The rigidity and strength of polyurethanes are foremost dependent on:

1. Type of cross-linking.

2. Number and type of polymer end groups-hydrogen bonding of the polymer.

In addition to these, other factors contributing to the structure-property relationship are (and of these very little is published in the literature):

3. Stiffness of chain units (limited rotational or configurational possibilities.)

4. Ease of rotation of chain segments.

Cross-linking is of primary importance in controlling polymer properties. A low degree indicates relatively few cross-links per unit weight of polymer, typical of elastomeric materials. It is doubtful that a high degree of cross-linking can be obtainable through vapor phase catalysis with any present day resin system. The concentration of effective catalyst at any given time is of a low order. The rapid diffusion of any exotherm produced because of the environmental requirements further decreases the tendency toward multi cross-links; however, cross-links sufficient enough to yield substantially strong polymer systems are capable of being produced as has been demonstrated. The approach should be to use a highly reactive functional group resin system and very fast acting catalyst systems.

Cross-linking in a urethane polymer system occurs through the active hydrogens bonded to the basic nitrogen. The two types of cross-links (linear and three-dimensional) can be illustrated in the following equations:

$$R-NH_2 \ + \ RNCO \ \longrightarrow \ R-NH\overset{\overset{\textstyle O}{\|}}{C}NHR \qquad \text{linear}$$

$$\text{and} \quad RNH\overset{\overset{\textstyle O}{\|}}{C}NHR \ + \ RNCO \ \longrightarrow \ R-N-\overset{\overset{\textstyle O}{\|}}{C}-NH-R \qquad 3-D$$
$$\underset{\underset{\textstyle NHR}{|}}{\overset{|}{C=O}}$$
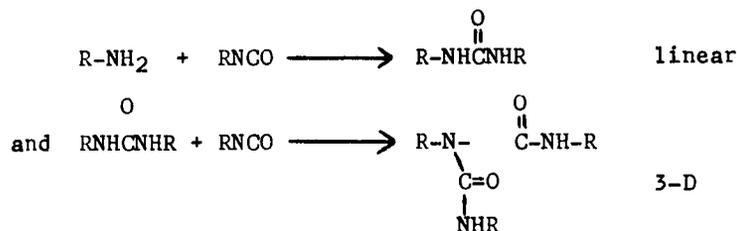
The initial equation involved the condensation of a free amine group with a isocyanate to form a stable disubstituted urea group which in turn reacts slowly with another isocyanate group through the active hydrogen

containing urea to yield a 3-D cross-linked biuret branch. The biuret bond is much weaker than the urea bond and too many of these will inherently weaken the thermal stability and rigidity of the polyurethane. This fact is verified experimentally when water cure systems are compared in which one is catalyzed by addition of a tertiary amine and the other is uncatalyzed. The urethane-uncatalyzed water system, although involving a longer cure time, retains higher physical strength and thermal stability. Addition of a tertiary amine favors biuret formation. Increased reaction temperatures (100°C) also enhance biuret formation.

Cross-linking may be controlled by the ratio of isocyanate groups to the total active hydrogen groups. This ratio must be greater than 1.0 to provide cross-linking. The addition of a trifunctional reactant will also contribute to the degree of cross-linking. Choice of catalyst can force certain reactions at accelerated rates as was pointed out above. In addition, catalytic effects may introduce other reactions such as trimerization and carbodiimide formation.

Thus, the successful structure-property relationship of a polyurethane is dependent on the type of cross-linking present in the polymer system and this factor is dependent on many parameters which have been and are being researched in this effort. The tensile strengths obtained would indicate a rather significant order of cross-linking attainable via vapor phase curing of the resin system. There is also an indication, from these results, that the molecular weights of the polymers evaluated probably are close to one another.

The number and type of polymer end groups and the manner in which they contribute to structure-property relationship is the second consideration to be discussed. The amount of hydrogen bonding contributed by the polymer system is dependent on the number and type of polar groups available. This factor likewise directly influences surface hardness and tensile and flexural strength. These bonds, sometimes called secondary chemical bonds, lack the strength of primary chemical bonds and are affected by increase in temperature and stress. In a system such as we have described, wherein the degree of cross-linking is not high, the influence of the secondary chemical bonds is at its greatest. This is a consequence of the proper orientation (geometric "fit") required for efficient hydrogen bonding. In a highly cross-linked polymer the multi-branching present restricts the spatial orientation thus the dipolar sites of the attracting groups are too far removed to interact.

The proper choice of prepolymer will also affect the structure-property relationship. Reactants having very limited rotational or configurational possibilities tend to rigidize polymer chains. The aromatic rings, with the ring itself a rigid unit or an acyclic structure with a rigid ring system, provide more inherent rigidity in the polymer, higher glass transition temperature, hardness and strength while reducing elasticity. Conversely, groups which impart a high order of flexibility, because of ease of rotation, favor softness, flexibility, elasticity, and lower melting points and glass transition temperatures. This can be verified by Table 4 where visual inspection of cured laminates were recorded. A decrease in the polyether polyol mole ratio or the inclusion of an aryl diol caused a greater degree of rigidity in the laminate.

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Initial synthesis of urethane modifications, wherein more built-in rigidity has been incorporated in the prepolymer, has produced films with superior hardness and tensile strength. The increase in rigidity was produced by using cyclic or aromatic diols where rotational freedom is restricted. Further effort will have to be undertaken before a final comparison can be obtained.

5. Experimental Work

Preparation of Moisture Cured Unreinforced Films

The urethane prepolymers were applied over glass panels using a draw bar set at 10 mil. The films were cured for 2 weeks at 75°F and 50% relative humidity. The films were removed from the glass panels and the physical properties were determined. The hardness of the urethane films were checked periodically with a Sward Hardness Rocker (Model C).

Preparation of Urethane Laminated Glass Fabric

The glass fabric employed was Style 181. The single ply laminates were prepared by spraying glass panels with a release agent and then applying the single ply of fiber glass. A 20-mil film of the prepolymer was then applied over the glass fibric and allowed to cure at 75°F and 50% relative humidity for 2 days. The 3-ply laminates were prepared in a similar manner.

Physical Test Procedures of Urethane Laminates

The flexural properties of the selected laminates were determined according to ASTMD-790. The test specimens were cut 3 inches long and 0.5 inches wide. The specimens were simply supported at each end and a normal load was applied midway between the supports. The crosshead speed was 0.02 in/min.

The flexural strength of the laminates were calculated from the following formula:

$$S = \frac{3PL}{2 bd^2}$$

where
    S = Stress, (psi)
    P = load, (lbs.)
    L = span, (in.)
    b = width, (in.)
    d = depth of beam, (in.).

The modulus of elasticity in bending was calculated from the following formula:

$$E = \frac{L^3 m}{4\,bd^3}$$

where

    E = modulus of elasticity in bending, (psi)
    L = span, (in.)
    b = width, (in.)
    d = depth, (in.)
    m = slope of the tangent to the initial straight line portion of the load
        deflection curve.

Tensile testing of specimens was performed on an Instron universal testing machine Model TT-C. The distance between the jaws (gage length) was 4 in., and the tests were conducted at a crosshead speed of .05 in/min. Calculation for the tensile strength of the specimens is as follows:

$$T = \frac{L}{Wt}$$

where

    T = tensile strength, (psi)
    L = load, (lbs.)
    W = width, (in.)
    t = thickness, (in.).

b. Epoxy

Epoxy resins have had a relatively recent history in the plastics industry. The ready availability of epichlorohydrin gave impetus to their commercialization. Most commercial epoxy resins are glycidyl-ether epoxide resins. These are normally prepared by reacting epichlorohydrin with substances having more than one hydroxyl group per molecule, the most usual substance being bisphenol A.

Depending upon the proportions of epichlorohydrin and bisphenol A used, epoxide resins of various molecular weight are obtained. The lowest molecular weight epoxy resin of this series is a liquid which is obtained by the reaction of a considerable excess of epichlorohydrin with bisphenol A. The following structure (I) illustrates this type.

(I)
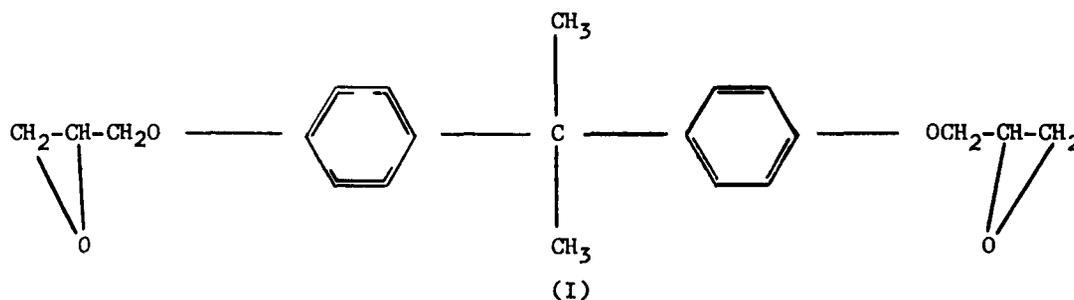
Diglycidyl ether of bisphenol A

A higher molecular weight epoxide resin of the series is a solid, obtained by the reaction of more nearly equal molar proportions of epichlorohydrin and bisphenol A. (II).

$$CH_2-CH-CH_2O \underset{O}{\diagdown} \text{—} \underset{}{\bigcirc} \text{—} \underset{CH_3}{\overset{CH_3}{C}} \text{—} \underset{}{\bigcirc} \text{—} OCH_2CH-CH_2O \text{—} \underset{}{\bigcirc} \text{—} \underset{CH_3}{\overset{CH_3}{C}} \text{—}$$

$$\underset{}{\bigcirc} \text{—} O-CH_2CH-CH_2O \text{—} \underset{}{\bigcirc} \text{—} \underset{CH_3}{\overset{CH_3}{C}} \text{—} \underset{}{\bigcirc} \text{—} OCH_2CH-CH_2$$
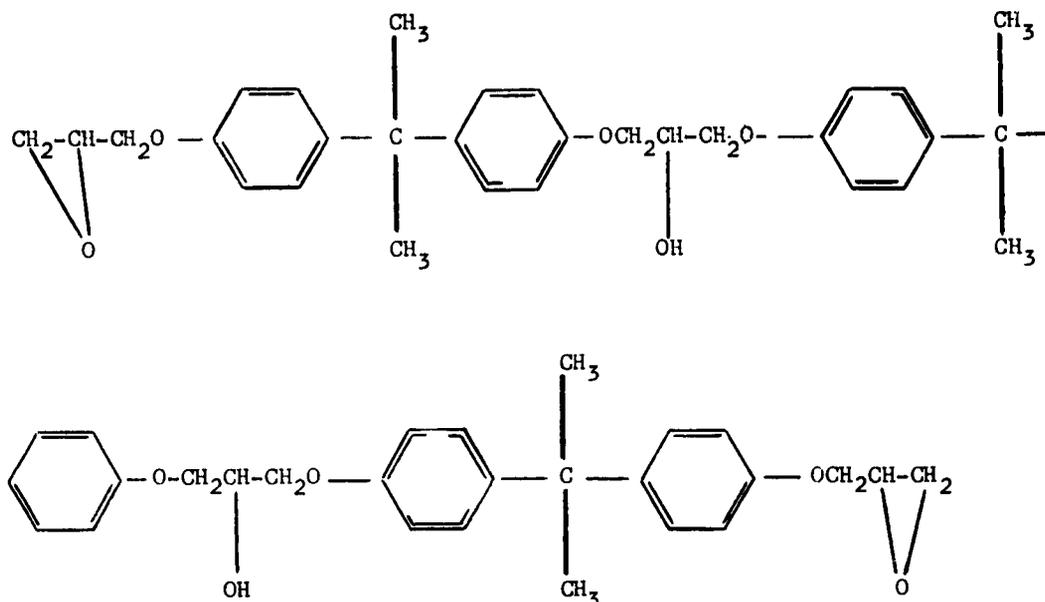
(II)

It should be noted that I and II have in common terminal glycidyl-ether type epoxide groups. The solid resins differ from the liquid resins in having hydroxyl groups along the chain. The ratio of I to II, in a base resin, determines the viscosity of the epoxy. Many of the properties of this polymer depend on the other linkages, the secondary hydroxyl groups, and the availablility of the epoxide groups on the ends of the chains. The importance of the terminal oxirane groups is great, as the degree of polymerization is low before cross-linking occurs. To obtain a hard durable plastic, cross-linking catalysts (which are termed hardeners) must be combined with the epoxy resins. These hardeners are usually amines, polyamides, acid anhydrides, Lewis acids, etc. An effective hardener, for example, a primary diamine, reacts according to the following equations:

$$CH_2 - CH - R - CH - CH_2 + NH_2 - R' - NH_2 \longrightarrow$$

$$CH_2 - CH - R - CH - CH_2 \, NHR'NH_2$$
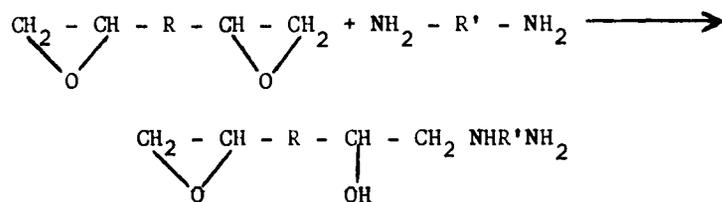
Actually, the cure consists of an initial production of linear chains followed by cross-linking chains until the molecular structure of the cured resin is highly complex. The active OH group is an intermediate compound which can be further linked. The largest use of epoxy resins is as film formers in surface coating formulations. The combination of properties such as the following:

1. Excellent adhesion to a wide variety of different surfaces,

2. Chemical resistance,

3. Curing without evolution of by-products at low or moderate temperatures, and

4. Low shrinkage on curing,

make epoxies extremely interesting for application of vapor phase curing of resin systems. Promising results were obtained with the epoxide resin intermediates as reported in an ASD report TDR-62-311 by T. L. Graham entitled "Expandable Rigidizable Structures." In that report it has been claimed that certain members (specifically the simple or low-molecular-weight bisphenol-A epichlorohydrin adducts) were found to completely rigidize on exposure to gaseous tertiary amines at room temperature.

We have also found the vapor catalyzed curing of an epoxy system to be operationally feasible. Our initial effort was to screen the commercially available resins and from these data choose the most likely systems to evaluate further. These resins and their compositions are listed below.

The following commercial epoxy resins were evaluated:

Shell

Epon 815	Simple adduct of bisphenol-A/epichlorohydrin diluted with butyl glucidyl ether, viscosity 5-6 poises.
Epon 812	Liquid epoxy resin, low equivalent weight high epoxy equivalent, viscosity 1-1.5 poises.
Epon 820	Adduct of bisphenol-A/epichlorohydrin diluted with phenyl glycidyl ether, viscosity 40-100 poises.
Epon 828	Same as above; no diluent; viscosity 100-160 poises.

Dow

Novolac DEN 438	Phenolic epoxy resins, no diluent; viscosity 300 poises.
DER 331	Low molecular weight epoxy resin based on bisphenol-A/ epichlorohydrin, viscosity 110-160 poises.
DER 332	Similar to 331, containing a higher percentage of the diglycidyl ether of bisphenol A; viscosity 64 poises.

FMC Corporation

Oxiron 2000   Epoxidized polyolefin liquid resins; viscosity 1800 poises.

Oxiron 2001   Low viscosity version of 2000; viscosity 760 poises.

Ciba

Araldite 502   Bisphenol-A/epichlorohydrin polymer containing a diluent; viscosity 30 poises.

Araldite 6010   Unmodified bisphenol-A/epichlorohydrin polymer; viscosity 95 poises.

DP-440   Non-burning liquid epoxy based on cycloolefinic compounds.

RDR-700   Consists of polyglycidyl ethers of polyhydroxy polyphenyls.

RDR-701   Consists of the triglycidyl ether of trihydroxydiphenyl; viscosity 113 poises.

The following curing agents were evaluated:

1, 3-Propylene diamine	Glutaric anhydride
1, 4-Cyclohexane bis (methylamine)	Pivalic acid/stannic chloride Lewis acids, PF_5, BF_3
Propionic anhydride	Borate esters

1, 3-Propylene diamine was the most successful curing agent used for vapor phase employment. 1, 4-Cyclohexane bis (methyl amine) was non-volatile at the conditions used (10-20 microns) and did not rigidify the impregnated materials. The anhydrides, pivalic acid/stannic chloride and borate esters proved ineffective.

For use as curing accelerators, triphenyl phosphite, tri-methoxyboroxine and the reaction product from adipoyl chloride and boric acid were evaluated and all found to exert a strong activating effect.

The following structural fabrics were used in evaluations:

Fortisan yarn fabric Style NW 372 (Celanese Fibers Co.)
Glass Fabric Style 181-Type E (Gustin-Bacon Manuf. Co.)
Raypan glass fluted panel Core Number 403, 233
(Raymond Industries)

The performance data of the various available systems is recorded in Table 7. These data were collected on samples cured at room temperature by direct mixing of catalyst and resin. It was felt that the most operable system under these circumstances would be most operable under conditions employing vapor catalysis. In this manner we were able to accomplish an evaluation of numerous resin-catalyst-accelerator combinations and record optimum concentrations of each component. Observations were:

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RESIN (50%)	CATALYST	MOLES OF CATALYST	CATALYST % BY WEIGHT BASED ON WT OF RESIN	CURING AGENT	MOLES OF CURING AGENT	CURING AGENT % BY WT BASED ON WT OF RESIN	GEL TIME (MIN)	SET TIME (MIN)(HARD TO TOUCH)	HARDNESS AT SET TIME (DUROMETER D SCALE)	HARDNESS AFTER 2 HOURS (DUROMETER D SCALE)
Epon 815 (Shell)	---	---	---	1,4-cyclohexane bis (methyl amine)[1]	0.14	40	55	90	60	80
	triphenyl phosphite[2]	0.0016	1		0.14	40	45	75	55	80
		0.008	5		0.14	40	30	60	55	80
		0.016	10		0.14	40	25	55	55	84
		0.024	15		0.14	40	25	55	55	84
		0.008	5		0.035	10	65	55	--	20
		0.008	5		0.053	15	40	70	15	80
		0.008	5		0.070	20	38	50	30-40	87
		0.008	5		0.088	25	35	50	30	86
		0.008	5		0.105	30	33	55	50-60	85
		0.008	5		0.175	50	35	75+	25	75
		0.008	5	1,3-propylene diamine[3]	0.034	5	--	soft after 69 hours	--	--
		0.008	5		0.068	10	35	55	72	87
		0.008	5		0.14	20	22	45	80(60 min)	80
		0.008	5		0.20	30	45	75	65	8C
		0.008	5		0.27	40	55	90	35	50-55
		0.008	5		0.34	50	65	soft after 69 hours	--	--
		0.008	5		0.098	14	70	85	48	85

TABLE 7. PERFORMANCE DATA OF EPOXY RESIN

Resin	Additive			Curing agent		40	30	32	
	Trimethoxy boroxine[4]	0.024	5	1,4-cyclohexane bis (methyl amine)	0.14				--
	----	--	--	Borester 8 (USB)[5]	0.03	20	only slight cure after 24 hours		--
	----	--	--	USB Curing Agent 110[5]	0.054	20	only slight cure after 24 hours		--
	----	--	--	Pivalic Acid[1]	0.098	20	no cure after 24 hours		--
Epon 812 (Shell)	SnCl4	0.0095	5		0.098	20	little cure after 24 hours		--
	----	--	--	1,3 propylene diamine	0.098	14	15	16	charred and decomposed / 78(approx)
	Triphenyl phosphite	0.008	5		0.098	14	5	6	78(approx)
		0.008	5		0.068	10	8	10	78(approx)
		0.008	5		0.034	5	NR after 7 hours		--
25g Epon 812 / 25g Epon 820		0.008	5		0.098	14	30	31	charred and decomposed
10g Epon 812 / 40g Epon 820		0.008	5		0.098	14	30	31	82(50 min) / 88(approx)
Epanol 55-B-40 (Shell)		0.008	5		0.098	14	--	--	rubbery after 24 hours
Epon 820 (Shell)	----	--	--		0.098	14	45	47	88(18 hours)
	Triphenyl phosphite	0.008	5		0.098	14	15	16	55(25 min) / 85+
Epon 828 (Shell)	----	--	--		0.098	14	48	55	70 / 70+
	Triphenyl phosphite	0.008	5		0.098	14	21	40	70 / 80+
DEN 438(87 pts)(Dow) Xylene(13 pts)	----	--	--		0.098	14	56	60	75(75 min) / 85+

TABLE 7. PERFORMANCE DATA OF EPOXY RESIN CONTINUED

Resin	Catalyst			Hardener					
	Triphenyl phosphite	0.008	5		0.098	14	12	13	78(23 min)	87
DEN 438 with 13 pts Acetone	Triphenyl phosphite	0.008	5		0.098	14	4	6	70(13 min)	87+
DER 331 (Dow)	----	--	--		0.098	14	65	70	70	82+
	Triphenyl phosphite	0.008	5		0.098	14	20	25	84(40 min)	88
DER 332 (Dow)	----	--	--		0.098	14	85	90	82(100 min)	88
	Triphenyl phosphite	0.008	5		0.098	14	20	25	83(35 min)	88
DER 334 (Dow)	----	--	--		0.098	14	85	90	78(100 min)	78+
	Triphenyl phosphite	0.008	5		0.098	14	22	25	83(40 min)	85+
Oxiron 2000 (FMC)	----	--	--		0.098	14	no cure after 18 hours			--
	Triphenyl phosphite	0.008	5		0.098	14	no cure after 18 hours			--
Oxiron 2001 (FMC)	----	--	--		0.098	14	no cure after 18 hours			--
	Triphenyl phosphite	0.008	5		0.098	14	no cure after 18 hours			--
Oxiron 2002 (FMC)	----	--	--		0.098	14	no cure after 18 hours			--
	Triphenyl phosphite	0.008	5		0.098	14	no cure after 18 hours			--
	----	--	--	Propionic anhydride[3]	0.062	16	no cure after 18 hours			--
	Triphenyl phosphite	0.008	5		0.062	16	no cure after 18 hours			--
RDR 700 (80 pts)(Koppers) Xylene(20 pts)	----	--	--	1,3-propylene diamine	0.098	14	42	50	57	80

TABLE 7. PERFORMANCE DATA OF EPOXY RESIN CONTINUED

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Resin	Additive								
RDR 701 (Koppers)	Triphenyl phosphite	0.008	5	0.098	14	12	13	75(30 min)	85
	----	--	--	0.098	14	16	25	75(35 min)	75+
Araldite 502 (Ciba)	Triphenyl phosphite	0.008	5	0.098	14	5	6	charred	charred
	----	--	--	0.098	14	75	95	20	80
Araldite 6010(Ciba)	Triphenyl phosphite	0.008	5	0.098	14	13	14	15(24 min)	85
	----	--	--	0.098	14	58	65	55	82
DP-440 (Ciba)	Triphenyl phosphite	0.008	5	0.098	14	8	9	80(20 min)	87
	----	--	--	0.098	14	46	63	20	65+
	Triphenyl phosphite	0.008	5	0.098	14	6	7	20(24 min)	87

1. Eastman Chemical Products, Inc.
2. Hooker Chemical Corporation
3. Union Carbide Chemicals Co.
4. Anderson Division of Stauffer Chemical Co.
5. U. S. Borax Research Corporation

TABLE 7. PERFORMANCE DATA OF EPOXY RESIN CONTINUED

1. Generally, the higher the average epoxy equivalent weight the greater the gel time; however, this is not true in every case.

2. Triphenylphosphite accelerated the curing of a resin up to a certain concentration. The maximum concentration is in the range of 5-10% by weight based on the weight of the resin.

3. The maximum rate of curè is obtained from using 0.07 moles of the diamine with 50 g. of resin, or 20% based on the weight of the resin.

4. The most effective concentration of propylene diamine is between 10 and 25% based on the weight of the resin, or 0.07 to 0.14 moles/50 g. of resin. (0.1 mole of amine per 50 g. of resin was chosen as optimum.)

The system showing the greatest promise was the Dow DEN 438 diluted with xylene. The viscosity of DEN 438 prohibits working with it in its commercial condition. Xylene was chosen as the diluent for the following reasons: (a) Its vapor pressure (760 mm at 138-144°C) is close to that of propylene diamine (760 mm at 135.5°C). It is then attractive to visualize a curing mechanism involving the replacement of xylene in the resin by propylene diamine as the xylene is vaporized and removed from the system. This gains support from the fact that acetone, which has a much higher vapor pressure than xylene, is removed more rapidly than xylene and only a surface cure of the resin is obtained, especially when the curing agent is pulled through the resin impregnated cloth; (b) xylene being a non-reactive diluent should not appreciably lower the cross-linking potential of the system as do reactive diluents; (c) the cure seems to be greater with xylene than when a resin of low viscosity (Epon 812 or DER-332) is used as a diluent, possibly because the curing agent is not able to penetrate before a surface cure is obtained.

It should be mentioned here that vapor curing by releasing propylene diamine from a Molecular Sieve (Linde 13X powder) loaded with water vapor was not as successful as with propylene-diamine alone. Because of this, and also because extra weight would be necessary (only approximately 20% absorption of the amine on the sieve), this concept was discarded.

Table 8 shows the results of adding various fillers to the resin. The fillers used were polyvinyl chloride (PVC), PVC plus vinylidene chloride, PVC plus vinyl acetate, PVC plus maleic anhydride, VMCH (contains free carboxyl groups), and VAGH (contains free OH groups). As before, the resin impregnated cloth was gassed with propylene diamine. The only fillers which gave an appreciable improvement in strength over those samples with no filler were PVC and VMCH, both showing a 38% increase in tensile strength. However, several factors seem to over-shadow this moderate improvement: (1) The increase in weight due to the filler; (2) The resin is harder to work with due to increased viscosity with the filler; (3) vinyl chloride resins tend to degrade under the influence of ultraviolet rays present in outer space.

DEN 438 (80 parts by weight)-xylene (20 parts by weight), the most operable system, was next applied to small prototypes of a space shelter. These shelters were fabricated from Raypan fluted panel core No. 403. All seams were sewn and sealed to restrict the catalyst loss. The shelter (100g) was impregnated with

Filler	Weight of Cloth[1](gm)	Weight of Resin[2](gm)	Cure Time (hrs)[3] at 20 ± 10 microns pressure	Weight Gain (+) or loss (-) (gms)	Tensile Strength lbs/in²	% Improvement over Sample with no Filler
---	5.10	4.99	17	-0.94	22,400	----
PVC (Geon 121)	5.06	5.39	18	+0.27	31,000	38
PVC + Vinylidene Chloride	5.07	6.76	18	-0.52	23,800	6
PVC + Vinyl Acetate	5.12	4.75	18	-0.33	22,400	0
PVC + Maleic Anhydride	5.02	5.70	17	-0.08	25,500	14
VMCH[4]	4.97	4.94	17	+0.20	30,900	38
VAGH[5]	5.02	5.51	17	-0.55	19,700	-12

1. In all cases Uniglass-Type E-Style 181 cloth was used.
2. In all cases a mixture of 20g. (DEN 438-80 parts; xylene-20 parts), lg. triphenyl phosphite and 5g. of filler were used to impregnate the cloth.
3. In all cases 10g. of propylene diamine were pulled through the sample bag.
4. Copolymer containing vinyl chloride, vinyl acetete and maleic acid in a ratio of 86:13:1 respectively; a Union Carbide Bakelite resin.
5. Copolymer containing 91% vinyl chloride and the remainder partially hydrolyzed vinyl acetate; a Union Carbide Bakelite resin.

TABLE 8. EFFECTS OF FILLERS ON AN EPOXY RESIN

an equal weight of resin and propylene diamine was allowed to pass through at a pressure of about 20 microns at room temperature. After 24 hours at this pressure the shelter was removed and found to be rigid enough to stand on (a similar eatment using DEN 438 (80 parts) - Acetone (20 parts) gave only a surface cure). An incomplete cure was obtained after only 15 hours. However, upon adding 10% by weight of the reaction product between boric acid and adipoyl chloride, complete cure was realized in approximately 7 hours. An attempt to increase the cure time by using trimethoxyboroxine as a vapor catalyst and 4,4'-diaminophenyl sulfone as a dormant cross-linking agent failed because of the decomposition of trimethoxyboroxine on heating.

Table 9 records tensile and flexural physical data on single and 3 ply glass 181 laminates saturated with DEN 438 (xylene) and cured with propylene diamine for 16 hours at room temperature and a pressure of 10^{-3} mm/Hg.

c. Polyester

Aropol 7200 Mc polyester, 30% solids in diallyl phthalate catalyzed with dimethyl aniline (1%) and .5% cobalt octoate was used to impregnate (38% resin content) a pre-formed cylindrical (6" diameter, 12" length) Raypan 403 constructed structure. A 15% by weight total of t-butyl peroxy isopropyl carbonate (Pittsburgh Plate Glass) which volatilizes at $25^{\circ}C$ at 10^{-2} mm/Hg was used in an attempt to cure the polyester system by peroxide vapor. After an 8 hour period there was   evidence of any curing. The heat dissipation by volatil- ization encountere. t these pressures will require a very active polyester- catalyst system. This approach although showing initial failure remains one of interest because of the physical strengths obtained from polyester cured laminates.

d. Phenyl Silanes

Vapor phase curing of a phenolic modified silane (Resinox SC-1013) showed no promise. Commercial applications of this type resin requires pressure lamination and extensive post curing cycles at elevated temperatures.

e. Furfural Resins

ADM's furfural based resins; Chem Rez 100A and Chem Rez 300, cure in seconds when catalyzed with 20% strong acid such as 85% H_3PO_4, catalyst A-31 and concentrated HCl. Evaluation of these systems for use in vapor curing techniques showed limited success. Single ply laminates of glass fabric 181 were saturated with Chem Rez 100A and Chem Rez 300 (50% resin content) and placed in a desiccator with concentrated HCl. After 20 hours the laminates were black, tack free, and non-rigid. After 48 hours tensile strengths were run on 1" x 4" samples. The data recorded in Table 10 indicates poor strength achievement. In addition the highly corrosive and toxic acidic vapors place a decided disadvantage on this system.

TABLE 9

Sample	Tensile psi	Flex psi	Modulus of Elasticity psi X 10^{-5}
1997-01	17,200	23,4ᴄ0	5.60
1997-02	17,200	22,250	4.99
1997-03	15,200	20,850	5.01

TABLE 9. PHYSICAL PROPERTIES OF EPOXY CURED GLASS LAMINATES

Sample #	Resin	Tensile psi
1945-63-1	Chem Rez 100A	8,500
1945-63-2	Chem Rez 300	4,000

TABLE 10 STRENGTHS OF SINGLE PLY

FURFURAL RLSIN-GLASS FABRIC LAMINATES

2. Plasticizer Removal

As this approach appeared to be most reliable and simple in operation,
it was evaluated as a rigidization system. Protective coatings for industrial
and architectural applications all operate to some degree on this method since
a 100% solid system has not been developed. The resin systems screened for
structural strength properties by plasticizer boil off techniques are the
following: (a) polyacrylic, (b) polyacrylic modified by the addition of styrene-
maleic anhydride copolymer and melamine resins, and (c) protein.

a. Polyacrylic

Initial investigation of an experimental ADM polyacrylic resin 5803-20-6,
containing 60.3% solids by weight diluted in a 75/25 xylene-butanol solution
was undertaken. This product impregnated on glass style 181 or Fortisan NW
372 and subsequently desiccated to 10^{-3} mm rigidified rapidly by plasticizer
release. The rigidified samples were coated with an extremely brittle, blistered
film which offered little strength. In addition the adhesion of the polymer
substance to both substrates was poor. The prepared samples were inadequate
for physical testing.

b. Polyacrylic, Styrene-Maleic Copolymer, Melamine Resin

Polyacrylic resin modified by the addition of a styrene-maleic anhydride
copolymer (3000 M-wt) and a melamine resin gave a plasticizer release system
which exhibited the most promising performance. The advantages of .this system
include: (1) relatively better adhesion to glass compared to the unmodified
polyacrylic resin, (2) reduction in blistering and frothing, and (3) a more
rigid surface. The adhesion of resin to glass was improved by synthesizing an
acrylic resin high in free carboxyl. The increased polarity attributable to
the carboxyl acid group increases surface adhesion of the resin to a substrate
such as glass. The rigidity afforded by removal of the plasticizer from this
system has been greatly improved by the addition of 20% by weight of styrene-
maleic anhydride copolymer and 5% by weight melamine-formaldehyde resin. For
ease of impregnation this mixture was solvalized with acetone and applied from
solution to give a highly uniform deposit of resin and thus a thin surface
film. This had the overall effect of decreasing the tendency of the resin to
blister during desiccation. Cure times employing vacuum conditions are under
two hours for maximum rigidity. Table 11 records tensile strengths from
single ply glass 181 laminates impregnated with the 3 component acrylic system.
As evidenced by the data some terminal cross-linking between the free carboxyl

-37-

of the acrylic and the anhydride of the SMA copolymer is no doubt occurring
with the amine containing melamine resin. Any source of heat will tend to
accelerate this tendency to form a molecular network leading to high hardness,
rigidity, and stability in the final product. Model aerospace structures
have been impregnated with this system and have been evaluated. Of the
plasticizer boil off techniques explored, this system shows optimum workability.

Sample #	Tensile psi	Flex psi
1997-19-1[1]	20,500	
1997-19-2[1]	19,047	
1997-19-3[1]	20,238	
1997-19-4[1]	18,750	
1997-17-1*	7,550	583

1. Single ply laminates glass satin weave 181 impregnated with
    modified acrylic system.

*   Single ply laminate glass satin weave 181 impregnated with
    polyacrylic resin 5803-20-6.

TABLE 11   STRENGTHS OF SINGLE PLY

ACRYLIC RESIN-GLASS FABRIC LAMINATES

c. Protein

The protein evaluated was ADM 303 isolated soybean protein which contains
about 95% protein and is best classified as a globulen (glubular protein) with
a molecular weight of 200-300,000. A 20% solids solution of isoelectric
potassium proteinate dissolved in water-glycerol solution (75-25%) was used
to impregnate glass fabrics. Free films of the proteinate were brittle. It
was found that successful laminates could only be prepared by application of
pressure and heat. Attempts to rigidify samples by plasticizer boil off in
a high vacuum (10^{-2} mm Hg) left surfaces with poor adhesion. Warping and
shrinkage of the desiccated films is a serious problem. Blistering and foam-
ing of the impregnated proteinate on glass fabric was a persistent problem
brought about by the inclusion of air in the slurred protein solution. A very
careful agitation reduced this problem and the use of anti-foaming agents
tended to eliminate it altogether.

The initial difficulties encountered with proteinate and modified
proteinate impregnants on glass caused a shift of emphasis to other systems
for evaluation; however, it is felt that natural products of this type, because
of their inherent physical properties, should still be of high interest.

3. Radiation Cure

Because of the PR specification for the development of a single system which would serve for the inflation and rigidization of structures in space and on earth, radiation cure was felt to be the most inoperable. The deployment of structures dependent upon ultraviolet, thermal, or other radiation for rigidization would add to the complexity of the task and be mechanically unreliable.

In addition, the space environment of high vacuum operation and high incident radiation may be inadequate for catalyzing vinyl unsaturation in the absence of an initiator and the presence of those same initiators may well promote polymer degradation if left in the polymer system.

SECTION 5

SPACE SHELTER

A. Design Concept

The extra-terrestrial human shelter design studied was a seven (7) foot diameter cylinder five (5) feet high, sealed with a floor and a semi-hemispherical roof such that the curved surface was two (2) feet high. Provision for human entry was to be provided. The entire shelter was to be composed of flexible honeycomb, self-rigidizable in a vacuum environment. The rigidized shelter would be capable of supporting 100 lb/ft^2 on the roof and would retain an internal pressure of 14 lb/in^2.

1. Shelter Strength Requirements

The compressive forces tending to crush the cylinder when evacuated are:

$$F = \frac{W}{A}A$$

where: W/A = Weight per unit area = 100 lb/ft^2

A = Area of roof surface = 38.5 ft^2.

This load can be expressed as lb/in of circumference or if the circumference is 264 inches,

$$F_c = \frac{3850}{264} = 14.5 \text{ lb/in}$$

Concentrated stresses occur at the junctions of the cylinder with both the roof and the floor. Refs. 15-17 present an analytical approach to determination of these concentrated stresses.

A much larger strength requirement is the ability to resist the tensile forces which tend to spread the cylinder open and to blow the top off when the shelter is inflated to 14 lb/in^2. This spreading force, per inch of height in the cylinder is:

$$F_c = \frac{PD}{2} \quad \text{or } 588 \text{ lb/in.}$$

Again, the concentrated stresses at the junctions with the roof and floor can be determined by the theory expressed in Refs. 15-17.

B. Structural Materials

An extensive search of the weaving industry revealed some unique three-dimensional expandable structural materials for aerospace use. It also brought out the fact that, at the present time, no one in the United States manufactures

a completely flexible true honeycomb core fabric. A true honeycomb sandwich material consists of an orderly array of cells oriented perpendicular to the skins and the optimum honeycomb is one in which the cells are woven integrally with the same threads as the skins. If a fiber or yarn such as fiberglass were used to weave this fabric, a flexible material would result which could then be impregnated with a suitable resin, folded and packaged, and at a later time inflated and rigidized. The results of the weaving industry search are presented in Table 12.

Several fabrics which closely resemble a true honeycomb weave were utilized in the current feasibility study. A flexible three-dimensional fiberglass material characterized by flutes integrally woven between skins was used with a resin in the construction of space shelters. The flute walls ran along the length of the fabric and were placed parallel to each other such that the flute cross-section was an isosceles triangle. Figure 1 shows this material in the unimpregnated state and figure 2 shows the same type material after impregnation, expansion, and cure.

Experiments with this material fabricated into structure models yielded a very strong cured product, with no particular problems from catalyst vapors escaping in localized areas.

A. Wimpfheimer and Bro., Inc., Stonington, Connecticut, suggested a scheme which would produce a configuration very similar to actual honeycomb. They proposed to drop threads, of any desired spacing and intensity, between two woven faces such that a series of squares would be arranged perpendicular to the two faces. The dropped threads could be dense enough that the resin system would tie them together to form essentially a solid wall. Since a development stage would have been necessary and the cost was appreciably higher than for Raypan material, it was decided to use the Raypan material.

Actual flexible honeycomb material was made by sewing glass tapes into square cores and then hand sewing faces onto the cores. This was a very time consuming and laborious procedure. However, enough of this type material was sewn to fabricate a five inch cube which was cured with a urethane system to show feasibility of this type of structural material.

C. Experimental Work

The development of the application techniques and methods to be used for vapor phase curing of resin impregnated flexible structural material, with the final goal the 7 ft. diameter shelter, proceeded along the following logical lines of approach.

1. Vapor curing of small impregnated patches.

2. Curing of small, simple, enclosed structures.

3. Curing of 1/10 scale models.

4. Curing of 1/2 scale models.

5. Curing of full size shelters.

FIRM CONTACTED	LOCATION	CONTACT	COMMENTS
Munsingwear	Minneapolis	R. Miller	No 3-D Available
Chicopee Mills	New Jersey	H.S. Merrell	No 3-D Available
Pacific Plastics	Seattle, Wash.	Don Grant	No 3-D Available
Honeycomb Corp. of America	Connecticut	F.J. Quinlan V.P.	Can't supply non-impregnated
Hexcel Products	California	E.C. Vicars, Tech. Dir.	Small quantities are available
Prewitt Plastics	Virginia	G. DeSantolo J.Z. Atkins	No 3-D Available
Honeycomb Products	Ohio	John D. Lincoln John Brandt	Has a way, - but it is proprietary
Wimpfheimer	Connecticut	H. Scheel J. Wimpfheimer Pres.	Nylon pile glass pile
"orst Richter	Pittsburgh	H. Richter	Suggested alternative
Hess Goldsmith	New York	Berg, Goldsmith, Hankin	No 3-D Available at this time
Goldsworthy Engineering	Torrance, Calif.	Brandt, Goldsworthy	
Johns-Manville	Ohio	S. Eaton T. Kizer	Asbestos Cloth
North American Asbestos Corporation	Chicago, Ill.	A. Jerome, V.P.	No lightweight asbestos cloth
American Asbestos Textile	Pennsylvania	M. Scanlan	No lightweight asbestos cloth
Bean Fiber Glass, Inc.	Jaffrey, N.H.	J. Manning W.J. Coleman	Can design a machine to weave 3-D core
Raymond Industries	California	P. Perkins	Fluted glass
Rand Development	Ohio	N. Binder	
Tolo Corporation	California	J. Lockshaw	Double Flutes

TABLE 12   WEAVING INDUSTRY SEARCH RESULTS

1. Patches

A series of epoxy-glass patches, saturated to a glass-resin ratio of about 1 to 1, were placed on a 4 inch diameter enbroidery hoop suspended from a small ring stand. A beaker of 1-3 propylene diamine was placed below the hoop and the assembly was surrounded by a 1 mil polyethylene bag closed at the top. After 18 hours in a 14" bell jar at about 0.3 mm Hg, the sample was removed and visually examined. Table 13 shows the results of 4 experiments. Comparing runs 2 and 4 shows that a larger amine surface area did not promote a better cure. Run 3 demonstrated that a larger supply of amine did effect a better rate of cure.

These experiments gave an indication of the cure time, the catalyst supply necessary, and the type of laminate which might be expected.

2. Simple Enclosed Structures

Knowledge gained from vapor phase curing of the patches was then applied to 6 inch cubic enclosed structures. A series of 6 inch cubes was prepared to further apply the vacuum cure of a shelter with vapor phase catalysis of a resin. 1-3 propylene diamine was supplied from a flask placed outside the cube with a rubber tube running to the interior of the cube. The materials tested were Raypan 233, a 3 dimensional glass fabric with a fluted core, and a Wimpfheimer Nylon # A.W., also a 3 dimensional fabric with 3/8" closely woven pile between the facings. 5% triphenyl phosphite was added to the epoxies to accelerate cure. Table 14 shows the results obtained from 5 runs.

A polyethylene bag was placed inside the cube in run 1 to learn the effect of retardation of the escape of amine vapor through the structure walls. Apparently this did not influence the rate of cure after 29 hours. Run 4 shows that a larger amount of amine is necessary to effect a cure in 16 hours.

Table 15 lists a series of 6 inch cube experiments and shows that poly-urethane resin impregnated onto Raypan fiberglass will give a satisfactory cure in 2 hours when used in conjunction with 25% water and 10% triethylamine. The amine and the water were placed in a 250 ml beaker inside the cube and the seam was tightly sewn. Runs 4, 5, & 6 demonstrate that polyethylene liners will probably not inhibit this type of vapor cure.

Figure 3 shows a fiberglass cube which was cured with a urethane resin and water vapor in about 2 hours.

These experiments revealed the fact that the seams or joints must be very well sealed in order to eliminate excessive catalyst loss. They also gave indications of the amount of catalyst needed, the cure times, and the structural strength which would be obtained.

3. 1/10 Scale Space Shelters

The next experimental step was the application of the vapor phase catalysis system to 1/10 scale models of the desired space shelter concept. As shown in the following sections, the material used was either nylon or fiberglass and the

RUN	EPOXY	% AMINE BASIS RESIN SOLIDS	REINFORCEMENT	RESULTS	SIZE OF AMINE BEAKER
1.	Epon 828	100%	181 Volan Glass Cloth	Good Cure	10 ml
2.	80% Den 438 in Acetone	37.5	Wimpfheimer 61-EO1	Not fully cured	10 ml
3.	80% Den 438 in Acetone	75.0	Wimpfheimer 61-EO1	Good Cure	100 ml
4.	80% Den 438 in Acetone	37.5	Wimpfheimer 61-EO1	Not cured	100 ml

TABLE 13.   VACUUM CURE OF EPOXY - GLASS LAMINATES

RUN	EPOXY	% AMINE BASIS RESIN SOLIDS	TIME IN VACUUM	RESULTS
1.	80% DEN 438 in Acetone	20	29 hours	Not Cured
2.	80 % DEN 438 in Acetone	20	29 hours	Not Cured
3.	Epon 815	86	16 hours	Good Cure
4.	80% DEN 438 in Xylene	29	16 hours	Not Cured
5.	80 % DEN 438 in Xylene	58	16 hours	Good Cure

TABLE 14. VACUUM EPOXY CURE OF 6 INCH CUBIC ENCLOSED STRUCTURES

RUN	REF.	% RAYPAN BASIS TOTAL WT.	% AMINE BASIS RESIN	% H₂O BASIS RESIN	% H₂O USED FOR CURE	TIME IN VACUUM*	LINING	% WEIGHT RETAINED BASIS INITIAL WT.	REMARKS
1.	5-14-63	50.0	0.5 DIA	34	27.8	2 hours	none		Good Cure
2.	5-15-63 D	40.5	"	"	37.5	2 hours	none	57	Good Cure
3.	5-15-63 E	37.0	0.5 DIA 10% TEA	25	44	3/4 hrs.	none	63	Good Cure
4.	5-20-63 F	40.0	"	25	40	1½ hrs.	1 mil poly outside	74	Good cure except for bottom edges
5.	5-22-63	45.0	"	"	55	2 hours	Poly inside and outside	79	Good Cure
6.	5-24-63	41.0	10% TEA	"	---	2 hours	Poly outside	75	Good Cure
7.	6-5-63	40.5	0	25	39	6.5 hrs.	none	69	6.5 hours - not cured. 2 days - cured

* pressure averaged from .20 to .30 mm/Hg

TABLE 1). VACUUM URETHANE CURE OF 6 INCH CUBIC ENCLOSED STRUCTURE

resin systems used were epoxies and urethanes. In nearly all cases, the seams of the structures were carefully sealed by gluing to avoid excessive catalyst loss.

A series of 1/10 scale model shelters were fabricated and vacuum cures were attempted using vapor curing techniques with both epoxy and urethane resins. Table 16 shows the results of these experiments. Five (5) percent triphenyl phosphite was added to the epoxy in Run 1. The placing of polyethylene bags as an inner or outer barrier was varied and is indicated on the table.

The resulting partial cure in Runs 1, 2, and 3, Table 16, show that insufficient amine was present. Considering the stoichiometric relation between DEN 438 with an epoxy equivalent of about 175 and 1-3 propylene diamine with an equivalent weight of 37, only 21% of amine is needed to complete the reaction. Obviously, a considerable portion of the amine was lost through the structure walls.

Runs 4 and 5 of Table 16 show that a water vapor cure of an isocyanate based resin in a vacuum is feasible. Difficulty was encountered in these two runs with the water freezing because of the heat required to vaporize the water. The shelters in these two runs, although not fully cured in two (2) days, became very rigid in about two weeks at room temperature and pressure.

Another series of experiments were conducted as a continuation of runs 2 and 3, Table 16. The amount of propylene diamine, which ' placed inside the structure in a 250 ml beaker, was increased in an effort) get a better cure. A small amount of water was added to assist inflation. Loss of the amine through the system has not been determined quantitatively. Table 16 describes the experiments which were conducted in a 14 inch bell jar. That table shows that a larger amount of amine did improve cure characteristics. The degree of cure at 16 hours was about the same as formerly obtained after 24-48 hours using less amine.

Table 17 shows some vacuum cures using a special epoxy cure accelerator, 1934-60 developed by ADM, used in connection with Epon 828 and a combination of Epon 828 and Epon 815. Best results were obtained in runs 2 and 3 utilizing a mixture of the two Epons. A control experiment omitting the 1934-60 was not conducted. The accelerator was a white granular material insoluble in the epoxy. It was applied by first mixing with equal parts of acetone and forming a slurry, then brushing it onto the resin soaked fabric.

Table 17 also describes an experiment using only Epon 815. A good cure was obtained on the inside in a short time, but the outside remained sticky. In this case Raypan fiber glass was used as reinforcement. The reason for partial cure could be due to escape of amine through the relatively loose weave of the fiberglass. Figure 4 shows a 1/10 scale fiberglass model, Figure 5 is a 1/10 scale nylon model, both were cured by vapor catalysis of an epoxy resin.

These experiments on 1/10 scale models further defined the fabrication techniques which appeared most promising, the cure times, the catalyst distribution problems, and the type of cured structure which could be expected.

REF.	REINFORCEMENT	RESIN	% TPP	% AMINE	% H₂O	AVE. PRESS. mm/Hg	TIME HRS.	REMARKS
4-15-HI	Wimpf. Nylon	80% DEN 438 in Xylene	6%	40%	2.2	.85	16	Fair Cure Amine used up.
4-17-HI	Wimpf. Nylon	"	6%	50%	2.2	.90	16	Fair Cure Amine used up.
* 4-18-63	Wimpf. Nylon	"	"	"	"	"	"	"
4-22-FHI	Raypan 233	"	"	"	"	1.7	"	Poor to Fair Cure.
1	Raypan 233	80% DEN in Acetone	6%	23.4		.20	26	Fair Cure. Poly inside and outside.
2	Raypan 233	80% DEN 438/ Xylene		23.4		.10	48	No poly in or out. Part Cure.
3	Wimpfheimer Nylon	80% DEN 438/ Xylene		23.4		.10	48	Bag inside with pin holes. Bag outside Part Cure.
4	Wimpfheimer Nylon	Arothane 1825-127			50%	.10	48	No poly inside or out. Part Cure.
5	Wimpfheimer Glass * #610OEO-1	Arothane 1825-127			50%	.10	48	Poly bag inside. Part Cure.

*Wimpfheimer fiber glass is similar in weave to the nylon previously described.

TABLE 16. VACUUM CURE OF MODEL SHELTERS WITH A VAPOR CATALYSIS SYSTEM

RUN	REF.	% REINFORCEMENT	% AMINE BASIS RESIN	RESIN	AVE. PRESS. mm/Hg	TIME HOURS	REMARKS
1	N-29-1	33.3% Wimpf. Nylon	40% Propylene Diamine	Epon 828 Accel.	35u	24	Not cured, soft ar l still wet.
2	N-31-1	33.5% Wimpf. Nylon	40% Propylene Diamine	Equal parts 828-815 Accel.	75u	7.5	Fastest cure so far.
3	N-33-1	31% Wimpf. Nylon	36.5% "	"	160u	5.5	Part cure. Another 2 hours probably would complete cure
4	N-31-2	50% Raypan Fiberglass #233	40%	Epon 815		4	Inside cured hard. Outside was sticky.

TABLE 17. VACUUM CURE OF MODEL SHELTERS WITH A VAPOR CATALYZED EPOXY

4. 1/2 Scale Space Shelters

A series of 1/2 size shelter models were fabricated and cured with the urethane resin system after it was revealed that the urethane system was a much faster curing system than the epoxy. Three 3-1/2 foot diameter houses were cured in a 5 foot vacuum chamber and three structures were cured at atmospheric pressure.

These shelters were fabricated from eight (8) panels of Raypan fiber glass sandwich material as shown in Figure 7. Each panel provided 1/8 of the circumferential distance at any particular point on the structure. Seams were made by overlapping the sandwich material and sewing; further reinforcement was provided by sewing a 1 inch glass tape on both sides of the seam. Forced inflation of the flutes resulted from making the outer skin of the sandwich material circumferentially longer than the inner skin. Early impregnation was accomplished by hand painting the resin onto the structural material.

a. Vacuum Cures

Table 18 describes the vacuum cured 1/2 scale shelter models. The procedure (except fo J-49-1) was to attach a water supply by way of a 2 inch tube to a polyethylene liner inside the impregnated shelter and place the entire unit inside the vacuum chamber as in Figure 6. The vapor pressure of the water was sufficient to inflate the structure and the polyethylene was porous enough that the water vapor was then "pulled" through the polyethylene as the chamber pressure was reduced. Chemical rigidization occurred when the water vapor catalyst came in contact with the urethane resin.

The house in J-49-1 did not fully inflate, probably because of insufficient water vapor or because the Raypan structural material was too porous. Run R-51-1 was changed by utilizing a 1 mil polyethylene liner and providing a larger water inlet. The total water was increased to 4 lb. Very good inflation was obtained but the structure tilted and became lop-sided. Greater care was exercised in placing the house in the chamber for R-53-1. Cure times ranged from 6 to 10 hours, the cured product is shown in Figure 7.

b. Atmospheric Cures

Two $3\frac{1}{2}$ ft diameter shelters were fabricated as above and were impregnated with the urethane resin system and cured under atmospheric conditions. Cure was affected by compressing atmospheric air and exhausting through the structure. Steam was injected into the air stream periodically. A vacuum technique, which will be described later, was used for resin impregnation of the structural material.

Table 19 describes three structures which were cured with steam and air in the atmosphere. R-59-1 describes a three ft. cube which was inflated with a small blower, and cured with a small steam generator. Steam was injected into the air stream for a period of 7 hours. After 12 hours, the resin seemed fully cured.

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VACUUM CURE OF 3½ FT. DIAMETER HOUSES *

REFERENCE	URETHANE WEIGHT	H2O WT.	TEA WT.	SIZE TUBING FROM CATALYST SOURCE	TIME IN CHAMBER	RESULTS
J-49-1	8 lb.	1.5 lb.	90 g.	0.5 in.	2 hr.	No in.t. ion. Structural material too porous. Not enough H_2O vapor.
R-51-1	8 lb.	4 lb.	90 g.	2 in.	2 hr.	House tipped in chamber. Poly bag liner. Cure time 6-10 hours.
R-53-1	8 lb.	4 lb.	90 g.	2 in.	16 hr.	House started to collapse on venting at 4 hours. Let run overnight. Good cure.

* Fabric weight of each unit was 14 pounds.

TABLE 18. VACUUM CURED 1/2 SCALE SHELTER MODELS

$3\frac{1}{2}$ FOOT STRUCTURES STEAM CURED IN THE ATMOSPHERE

REFERENCE	URETHANE WEIGHT	CONFIGURATION	STEAM SOURCE	RESULTS
R-59-1	14 lb.	Cube	Low volume generator 7 hours	12 hour cure. Good inflation shortly after impregnating fiberglass.
R-61-1	14 lb.	House with precured door	40 gal/hr pressure steam generator	Did not inflate. 24 hours after impregnating with resin.
R-62-1	13 lb.	House no door	40 gal/hr pressure steam generator	Good inflation shortly after impregnating. Six hr. cure. 2000 cfm air blower.

TABLE 19. ATMOSPHERIC CURED 1/2 SCALE SHELTER MODELS

R-61-1 describes a 1/2 scale model which was fabricated with an elliptical door. The door had been pre-rigidized as had a 2 inch section around the opening to serve as a framework. A neoprene gasket was used for a seal. After impregnation, the structure was packaged in a vapor barrier material package (figure 8). The package was flushed with dry nitrogen to eliminate any chances of water vapor remaining in contact with the resin. This unit did not inflate, probably because resin had drained from the upper portion of the packaged impregnated structure. The porosity of the fabric was such that without complete resin saturation, it would not hold sufficient pressure to cause inflation.

R-62-1 describes an experiment which was similar to R-61-1 except for the time delay between impregnation and cure and a slight increase in the output capacity of the inflation blower. This house inflated nicely and was cured in about 6 hours. The inflated and cured stages are shown in Figures 9 and 10 respectively.

5. Full Size Shelter

Two 7 ft. diameter shelters were fabricated, in a manner similar to the 1/2 scale models, with Raypan fluted core fiberglass material. These structures were lined with polyethylene to reduce porosity and packaged as in Figure 11 for transportation to Wright-Field. The entire structure weighed about 50 lb. before impregnation.

Vacuum impregnation was accomplished by placing the dry structure inside a flexible plastic film and sealing the film. A vacuum pump was connected to one side of the enclosed package and the other side of the package was connected to a resin supply. About 30 lb. of urethane resin solids were siphoned into the package and external pressure pressed the package tightly against the structure as a vacuum was pulled on the flexible plastic package. This procedure forces the resin evenly throughout the structure. This system is attractive because the resin is never exposed to moist air, the structure is packaged and can be sealed in a vacuum immediately after impregnation, very even distribution of the resin results, no elaborate equipment is needed, no resin is wasted, and structure size does not appreciably affect the method. This impregnation set-up is shown in Figure 12.

The impregnated structure was then placed in the 16 ft. diameter Wright-Field 150,000 ft. altitude chamber. The water/amine catalyst supply which was outside the chamber and is shown in Figure 13, was connected to the collapsed shelter and thermocouples were attached at various points for temperature monitoring. As the chamber pressure was reduced, the shelter inflated from residual air entrapped in the polyethylene liner. Water vapor was then supplied for 6 hours at which time it was necessary to discontinue the experiment. Approximately the upper 1/2 of the shelter was cured, but the lower 1/2 allowed the shelter to collapse.

The experiment was duplicated on the following day, October 11, 1963. A cable was connected to the top of the collapsed structure so the shelter could be kept from tipping during inflation. A good cure was obtained in about 8 hours (Figure 14) and the structure was sufficiently rigid to support a man's weight at any point on the roof surface.

The packaged volume of this structure was about 2 ft^3. The expanded volume was about 250 ft^3 or an expansion ratio of about 125.

SOLAR COLLECTORS

A. Background Information

A solar energy collector designed to satisfy the requirements for aerospace application must be packageable in a small, lightweight volume with subsequent deployment into a large, efficient, and long life energy conversion unit. Ref. 18 compares and describes six (6) different methods of approach to solar collector design and fabrication. Among the problems discovered most frequently were heavy weight, large packing volumes, "orange peel" effect on the reflective surface, and mis-formations in the paraboloidal surface.

1. Paraboloid

A paraboloid (as shown in the figure below) can be fully defined by the rim diameter and the rim angle.
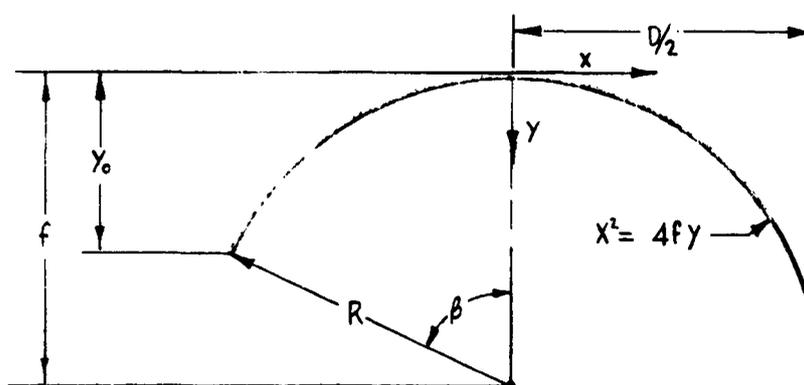
In polar co-ordinates, with the focal point as the origin, a parabola can be expressed as:

$$R = \frac{2f}{1 + \cos \beta}$$

with the symbols defined above.

Since $R \sin \beta = \dfrac{D}{2}$

$$f = \frac{D}{4} \; \frac{(1 + \cos \beta)}{\sin \beta}$$

and the depth of the paraboloid is:

$$yo = f - R \cos \beta$$

$$yo = \frac{D}{4} \frac{(1 + \cos\beta)}{\sin\beta} - \frac{D}{2\sin\beta} \cos\beta$$

$$yo = \frac{D}{4\sin\beta} + \frac{D}{4} \frac{\cos\beta}{\sin\beta} - \frac{D}{2} \frac{\cos\beta}{\sin\beta}$$

$$yo = \frac{D}{4} \frac{(1 - \cos\beta)}{\sin\beta} .$$

In cartesian co-ordinates the equation of the parabola is

$$4 \, fy = x^2.$$

Differentiating implicitly gives:

$$4 \, f \, dy = 2 \, x \, dx$$

or $\frac{dy}{dx} = \frac{2x}{4f} = \frac{x}{2 \, f}$

which is the slope of the parabola in any plane through the axis of rotation.

2. Paraboloid Fabrication

The surface of a liquid in a container rotating with constant angular velocity about a vertical axis will form a paraboloid of revolution with latus rectum of 2 g/w^2 where g is the acceleration due to gravity and w the angular velocity in radians/sec. The focal length of the paraboloid then depends only on the angular velocity. A resin system distributed over the surface of the rotating liquid offers a possibility of producing a mold for fabrication purposes.

What appears to be the most interesting approach to the fabrication of a parabolic reflector is preforming a plastic film over a mold by vacuum and heat methods. The formation over a mold can be done very satisfactorily with a polyester film and subsequent metallizing will provide a good reflective surface.

Another approach might be to create a pressure differential across a film that is restrained with a circular ring. By varying the film thickness, and hence the amount of stretch at various points, it may be possible to form a paraboloid with this pressure differential.

3. Paraboloid Corrections

A perfect "laboratory" paraboloid will not retain this exact shape during rigidization in a space environment. Some of the deformation factors which must be accounted for in the design are:

a. Inflation pressure

b. Rigidization material exothermic heat

c. Temperature gradients

d. Release of inflation pressure

These deformations all appear to be small and can easily be accounted for in the initial design.

4. Paraboloid Accuracy

An optical inspection is a major factor in the satisfactory design of a parabolic reflector. The geometric characteristics of the reflective surface can be determined to a fair degree of dependability with a relatively simple, but carefully executed and necessarily laborious experiment. By controlling the point (small area) on the reflective surface that a ray of parallel light is allowed to strike, and surveying the reflected spot at the focal point, a fair idea of the geometric accuracy can be obtained. Of course, the overall efficiency of the collector can best be obtained through calorimetric tests.

B. Structural Materials

The weight requirements of the solar collector, 0.2 lb/ft^2 maximum, suggested that a very light weight woven material would have to be incorporated into the entire design. It also appeared desirable to have a somewhat elastic material to provide better formability to the desired shape. Nylon, which can be woven as a very light weight material and has some elasticity, appeared promising.

An extensive review of available literature on space effects on nylon material revealed that nylon would satisfy the requirements of structural material for a solar collector. The resin-structural material compatability was tested with the types of resin to be used and was found to be satisfactory.

The special weave made by A. Wimpfheimer and Bro., Inc., Stonington, Connecticut, was two nylon faces each of about 3 ounces per square yard woven into an integral unit by rows of drop threads 5/8 inch long running in one direction. The rows were spaced about 1/2 inch apart. The total weight of the structural material is about 10 ounces per square yard. Figure 15 shows this material in the unimpregnated state. Figure 16 shows the same material after impregnation and cure.

C. Solar Collector Design

The design which was settled upon can be generally summarized as a pre-formed aluminized Mylar film coated with a flexible layer to absorb "show-through" and act as a bond between the Mylar and the structural-rigidizing material. The structural material could be rigidized with any of the vacuum adaptable resin systems; this design was used with a plasticizer boil-off system and the vapor cured urethane system. The three main portions of the design. the Mylar reflective surface, the bonding layer, and the structural material will be discussed in general in the next section.

1. Mylar Reflective Surface

The Mylar reflective surface used in this study was pre-formed by holding a f''m in place with metal rings and creating a pressure differential across the

film. (Figure 17). The pre-formed shape very nearly approximated a paraboloid. This work was essentially all done with 3 mil Mylar film to aid in eliminating the "show-through" problem.

2. Bonding Layer

An extensive series of experiments was conducted to arrive at a satisfactory method of bonding the structural material to the Mylar. These experiments will be discussed in a later section.

3. Structural Material

Attempts were made to pre-form the structural material to the same shape as the reflective surface in order to eliminate any distortion effects which the structural material might have on the reflective surface. Effort was applied toward pre-forming the back and causing it to hold the pre-formed shape with a coating of flexible resin. Those experiments will be discussed in the following sections.

D. Experimental Work

The development of fabrication and rigidization techniques followed a pattern of application to 8 inch models with subsequent revisions until the system appeared satisfactory, and then scaling up to a 2 ft. model for further revision. As new ideas were incorporated into the design, it was periodically necessary to perform preliminary study with the 8 inch models. The experimental work therefore did not necessarily proceed in order from 8 inch models, to 2 ft. models, and then to 5 ft. size, but this discussion of experimental work will be broken down in that order for clarity of reporting.

1. 8 Inch Models

Early efforts were directed toward eliminating the "orange peel" effect obtained when a backing material was bonded to a plastic film. A diaphragm tester was used to "blow a bubble" from films and various backing materials were placed over the bubble surface, impregnated with a resin system, and cured. Table 20 shows the different tests made and a brief discussion of results.

Initial attempts to rigidize the bubble were made by laying 181 Volan glass cloth over the film and rigidizing with an epoxy. The finished rigidized composite had severe show-through (a thin film was used) and warped in the weave direction of the glass cloth. Attempts were then made to rigidize the bubble by laying thicker material (Wimpfheimer AW Nylon) over a thicker film and rigidizing with an epoxy. The thicker film eliminated much of the show-through and the thicker backing material eliminated the warp. Attempts were then made to rigidize a film-epoxy combination by pre-forming the backing material, using loose fitting backing material, placing cushioning material between the film and backing material, and pre-cutting the backing material for a better fit.

Experiment No.	Type of Aluminized Mylar	Thickness of alum. film	Reinforcement on Back of Aluminized Film			Resin System Used		Results and Remarks
			1st layer	2nd layer	3rd layer	Resin	Curing Agent	
I-1	3M Aluminized Polyester film 1 side	.5 mil	181 Volan glass cloth			Epon 815 4 pt.	Epon T-1 1 part	Lost power discontinued
I-2	Mylar 1 side Aluminized	.5 mil	181 Volan glass cloth			Epon 828 5 pt. Tri-phenyl 1 part	Epon 1 part	Good bond, but show through (Orange-peel)
25-I	DuPont Mylar Aluminized 1 side	3 mil	Wimpf-heimer Nylon			Epon 815 80 gm	Epon T-1 20 gm	Nylon was placed over Mylar and formed with Mylar to shape. Very good, only a small amount of show through. Only fair bond.
26-I	DuPont Mylar Aluminized 1 side	3 mil	Wimpf-heimer Nylon			Epon 815 80 gm	Epon T-1 20 gm	Nylon was placed loosely over Mylar and formed with Mylar to shape. Better than 25-I. less show through. Better bond.
27-IV	DuPont Mylar Aluminized 1 side	.2 mil	Wimpf-heimer Nylon			Epon 815 80 gm	Epon T-1 20 gm	Nylon was preformed by soaking in water and hot air drying over desired shape. Nylon was then placed over Mylar and saturated with resin before inflating to shape.

TABLE 20. BENCH CURED 8 INCH SOLAR COLLECTORS

Experiment No.	Type of Aluminized Mylar	Thickness of Alum. Film	Reinforcement on Back of Aluminized Film			Resin System Used		Results and Remarks
			1st layer	2nd layer	3rd layer	Resin	Curing Agent	
28-II	DuPont Mylar Aluminized 1 side	3 mil	Wimpf-heimer Nylon			Epon 815 80 gm	Epon T-1 20 gm	Mylar was pre-formed by stretching beyond desired shape. Nylon was pre-formed as in 27-IV. Best surface yet.
28-I	DuPont Mylar Aluminized 1 side	3 mil	Light-weight silk	Wimpf-heimer Nylon		Epon 815 80 gm	Epon T-1 20 gm	Same procedure as 27-IV, except no heat was used to cure resin and silk was placed between Mylar and Nylon. Only lot of show-through. Only fair bond.
2-1	DuPont Mylar Aluminized 1 side	3 mil	Kleen-ex	Wimpf-heimer Nylon		Epon 828 80 gm	Epon T-1 20 gm	Kleenex was not stretched but was placed over Mylar. Some wrinkles were caused because of this. Nylon was pre-formed with heat.
3-1	DuPont Mylar Aluminized 1 side	3 mil	Kleen-ex	Cloth NW 372	Wimpf-heimer fiber-glass untreated 6100-EO-1	Epon 828 120 gm	Epon T-1 30 gm	Kleenex was stretched with Mylar. Cloth and Wimpf-heimer fiberglass were cut to shape with a 1¼" piesection cut out.

TABLE 20. BENCH CURED 8 INCH SOLAR COLLECTORS CONTINUED

Experiment No.	Type of Aluminized Mylar	Thickness of Alum. Film	Reinforcement on Back of Aluminized Film			Resin System Used		Results and Remarks
			1st layer	2nd layer	3rd layer	Resin	Curing Agent	
3-II	DuPont Mylar Aluminized 1 side	3 mil	Fiber-glass mat	Wimpf-heimer fiber-glass	untreated	Epon 828 80 gm	Epon T-1 20 gm	Fiberglass mat and Wimpfheimer were cut to shape with 1½" piesections and placed over Mylar.
13-I	3M Aluminized polyester film 1 side	.5 mil	Wimpf-heimer untreated fiber-glass			ADM 100 gm Tri-P-phate 5 gm	Amine 20 gm	Completely saturated cloth. About 20 min. later Mylar burst. Removed fiberglass and placed new layer of Mylar in jig.
12-I	DuPont Mylar Aluminized 1 side	3 mil	Wimpf-heimer untreated fiberglass			ADM 100 gm Tri-P-phate 5 gm	Amine 20 gm	Discontinued when Mylar burst. Apparently too much heat.
22-III	DuPont Mylar Aluminized 1 side	3 mil	Wimpf-heimer Nylon			ADM 759 Tri-P-pnate 3.75 gm	Amine 10 gm	Mylar pulled away - wrinkles in Nylon not filled by resin.

TABLE 20. BENCH CURED 8 INCH SOLAR COLLECTORS CONTINUED

It appears at present that the most satisfactory design will be a fairly thick layer of pre-formed metallized film, a cushion backing, and a layer of lightweight honeycomb structural material. A torus will retain the inflated shape due to pressure inside a conical or spherical cover film while the structural material is rigidizing. The cover film will be removed after rigidification.

Preliminary investigations show that a bubble surface in a film is very close to a paraboloid. Slight modification may make it possible to pre-form a reflective surface in this manner.

Table 21 describes the work done in an effort to find a method of bonding the structural material to the Mylar. In this set of experiments, three bonding materials were considered.

1. GE RTV 102, a silicone rubber adhesive

2. A polyvinyl alcohol, isopropanol, water emulsion

3. Epoxy

The RTV 102 provided a good bond, but was not sufficiently stiff to prevent fabric show through. The polyvinyl alcohol emulsion designated N-42-1 was rolled on the Mylar with a hard rubber roller and allowed to air dry. A good bond was then obtained between the Mylar and the epoxies. A fast cure epoxy system was used in order that more experiments could be conducted in a given time. It was thought that if a good bond was possible with a fast cure rigid resin, an equal or better bond would result with a slower curing, flexible system. This later proved to be correct.

In all cases the bonding material was first applied to the Mylar by brush and allowed to dry. The epoxy was next applied and cured. The structural material was coated with epoxy and placed over the film. Resin was then soaked onto the fabric for rigidization.

Three 8 inch solar collectors were bench cured using flexible formulations of unsaturated polyester resins as a cushioning material. ADM's polyurethane, 1988-19 was impregnated into the structural material for rigidification in order to demonstrate the usefulness of a cured urethane. Table 22 describes these runs. The work in Table 22 shows that an unsaturated polyester flexible resin is a candidate for use as a backing cushion. The 601 was very flexible and tough.

Two very flexible epoxy systems were brushed on films of emulsion treated Mylar. Adhesion to the Mylar was very good. Two difficulties encountered were "fish eyes" appearing in the cured film, and sagging of the wet resin on the curved film surface. Both of these problems were decreased by the addition of GE's SR-82, an anti-surface agent intended to reduce surface tension, and a small amount of Cab-O-Sil to prevent sagging. Table 23 describes 4 collectors, both vacuum cured and bench cured, using a flexible epoxy film. No attempt was made to control film thickness in these experiments but this can readily be done.

In run 5, the epoxy film was brushed on a flat piece of Mylar. After cure, the coated Mylar was formed into a bubble resulting in small wave lines where the resin was excessively strained. The flexible epoxies investigated were Shell's 872-X-75 and Union Carbide's ERL 2795. A very good surface could probably have been obtained in Run 5 using straight 872-X-75. Good bonds between the Mylar and the epoxies were obtained in all runs.

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TABLE 21. BENCH CURED 8 INCH SOLAR COLLECTORS USING EPON 815

Exp. No.	Cushion and Structural Backing Materials			Resin System	Curing Agent	Results and Remarks
	1st Layer	2nd Layer	3rd Layer			
4-8-I	Kleenex Tissue	Kleenex Tissue	Wimpf. Nylon	Epon 815	Epon T-1	Pre-formed nylon. Saturated nylon in jig before expanding to shape. Result. show through - no bond.
4-9-I	Kleenex Tissue	Kleenex Tissue	Wimpf. Fiber-glass	Epon 815	Epon T-1	Mylar did not stick to Kleenex except in a few places. Show through where it did stick.
4-11-I	Eponal #55-B-40	Wimpf. fiber-glass		Epon 815	Epon T-1	Allowed Eponal to cure overnight, however, too heavy a layer will not cure completely. Also air bubbles formed in Eponal.
4-14-I	Mylar adhesive Dupont #46971	Wimpf. fiber-glass		Epon 815	Epon T-1	Adhesive was cured overnight before forming film to shape. Results: Out of shape, must have been due to heat retained by fiberglass.
4-15-I	Epon 828 Tri-PP Epon T-1	Epon 828 Tri-PP	Wimpf. nylon Pre-formed.	Epon 815	Epon T-1	Results: No show-through, no bond.

Exp. No.	Cushion and Structural Backing Materials			Resin System	Curing Agent	Results and Remarks
	1st Layer	2nd Layer	3rd Layer			
4-25-I	GE RTV 102 adhesive	Wimpf. nylon pre-formed		Epon 815 Tri-PP	Epon T-1	No bond, roughness from RTV showed through.
4-29-I	GE RTV 102 adhesive	Epon 828 Tri-PP Epon T-1	Flexible Poly-urethane open cell	Epon 828 Tri-PP Cab-O-Sil	Epon T-1	Result: Lots of show-through, heat warped collector out of shape.
5-8-I	Emulsion N-42-1	Epon 828 Tri-PP Epon T-1 (2 layers of above)	Nylon Wimpf.	Epon 815 Tri-PP	Epon	Each layer was allowed to cure. Part of final resin was placed inside pre-formed nylon, the rest over the nylon. Result: Perfect.
6-7-I	Resin #601 MEKP	Nylon			Water TEA	The flex resin had air bubbles which show through. Fair bond. Backing warps.

TABLE 21. BENCH CURED 8 INCH SOLAR COLLECTORS USING EPON 815   CONTINUED

Exp. No.	Cushion and Structural Backing Materials		Resin System	Curing Agent	Results and Remarks	
	1st layer	2nd layer			Cushion	Urethane Backing
6-3-63	Emulsion Co-Rez 316 MEKP 6% Ccbalt.	Wimpfheimer Nylon	Urethane	0.5% DMLA 5% H_2O	Cheesy – not tough enough.	Not rigid.
6-7-I	Emulsion Co-Rez 601 2% MEKP	Wimpfheimer Nylon	Urethane	0.5% DMLA 5% H_2O	Pattern of knit good, tough.	Rigid, warped.
6-8-3	Emulsion Co-Rez 601 2% MEKP	Wimpfheimer Nylon	Urethane	0.5% DMLA 5% H_2O	Wavy from nylon, good.	Rigid; best surface of 3.

TABLE 22. BENCH CURED 8 INCH SOLAR COLLECTORS WITH POLYESTER FLEXIBLE CUSHION

Run	Ref.	Flexible coatings on back of 3 mil aluminized Mylar		Fabric bond to film	Resin to Rigidize	Vacuum	Results
		1st Coat	2nd Coat				
1	N-41-1	Epon 872-X-75		RTV 102	ADM Acrylic	2 hours 3 mm	Fish eyes. One of the better vac. cures. Some show through.
2	R-41-1	872-X-75 1% SR-82	872-X-75 1% SR-82	Epon 815	Epon 815	None	No fish eyes. Good surface. Wrinkles from nylon backing.
3	R-42-1	Epon 872-X-75		RTV/Tol 1/1	Epon 815	None	No fish eyes. Good surface. Wrinkling from nylon.
4	R-42-2	Epon 812-80 828-20	Epon 872-80 parts 828-20 parts	872-80 828-20	Epon 815	No	Same as above. Good bond to Mylar in all cases.
5	R-42-3	Epon 812-80 828-20		872-80 828-20	Epon 815	No	Good surface but stress lines from the epoxy blend.

TABLE 23. 8 INCH SOLAR COLLECTORS WITH EPOXY FLEXIBLE CUSHION

An improved ADM acrylic formulation was used to rigidize a series of solar collectors in vacuum. Resin formulation was as follows:

ADM Acrylic 5803-30-17	100 parts
Styrene-Maleic Anhydride Adduct	20 parts
Melamine-formaldehyde resin	4 parts

In this series GE's RTV 102 was tried both as a bonding agent and a cushioning film to avoid structural fabric show through. The RTV 102 was diluted with ADM's polyurethane 1988-19 and toluene to make it more workable. Uncut nylon velvet with 3/8 inch pile was used as the backing material after pre-forming it with heat and acetone. Surfaces obtained were wrinkled and showed the weave of the nylon. Rigid cures were not obtained, resulting in deformation of the paraboloid structure. The collectors were suspended in a set of 8 inch metal rings. A cover film with a valve served to hold pressure against the aluminized film. Results of these experiments are shown in Table 24. They indicate that the RTV is probably too flexible to elimin.re show-through. It does, however, provide a very good bond with Mylar.

A final series of 8 inch solar collectors yielded good surfaces except for some show-through from the nylon flutes. Complete elimination of show-through using flexible epoxy systems was achieved by fabricating with a cushion having four layers; however, that produced excessive weight in the final cured structure.

The backing material used in the collectors consisted of the specially woven three-dimensional nylon fabric with 5/8" drop threads connecting the faces. A variety of epoxy combinations was tested for flexibility and elimination of surface show-through. Blends of Epon 872-X-75 and Epon 828 or 820 and mixtures of Versamide 125 and Epon 828 or 820 were tested. Two percent Cab-O-Sil was incorporated into the epoxy systems to prevent sagging and formation of a resin torus on the blown film. In order to prevent "fish eyes", two surface active agents were tested. These agents were PC 1344 Monsanto Chemical Co. and SR-82, a product of General Electric's Silicone Division. PC 1344 was selected on the basis of best performance.

Table 25 describes 8 inch diameter vacuum cured collectors, some of which were cured at 5×10^{-5}mm Hg. In order to more closely simulate space conditions, the water and triethylamine were introduced into the urethane impregnated nylon from outside of the bell jar. When this was first attempted, the core did not expand because the resin solvent had been removed during pump down of the chamber. This resulted in too great a porosity to hold sufficient pressure for structural material inflation. This condition was greatly improved by first impregnating the nylon with urethane and desiccating for 20 to 30 minutes in a low vacuum, then applying a second coat of urethane to the fabric. Experiments J-73-1, J-62-1, and J-76-2 demonstrated that better core inflation resulted when employing this two coat technique. Those three experiments were conducted in a vacuum facility at Wright-Patterson Air Force Base, Ohio. A thermocouple indicated that the collector temperature was 75°C. Internal pressure was controlled between the reflective surface and the cover film from outside the chamber.

2. 2 Ft. Models

Knowledge gained from the 8 inch model experiments was then applied to 2 ft. models.

Run	Ref.	Cushion and Bond	Time in Vacuum	Average Pressure	Bond	Results
1	J-34-2	RTV 102	2 hours	3 mm	Fair - not uniform.	Wrinkles. Fair cure.
2	J-35-1	RTV 102	2 hours	1 mm	Fair - not uniform.	Same as in Run 1. Tried to apply RTV more evenly.
3	J-35-2	RTV in urethane	2 hours	0.75 mm	Poor	Surface wrinkled. Poor.
4	J-36-1	RTV/Toluol 50/40	2 hours	.40 mm	Good	Good cure - wrinkled surface.
5	J-37-1	RTV/Toluol 50/50	1½ hours	.78 mm	Good	Good cure but did not hold its shape when removed from ring.

TABLE 24. VACUUM CURED 8 INCH SOLAR COLLECTORS

Exp. No.	Cushion and Structural Backing Materials			Resin System	Curing Agent	Results and Remarks
	1st layer	2nd layer	3rd layer			
R-45-1	4 coats of Epon 872 20 g 828 20 *		preformed nylon bonded with 4th epoxy layer	100 g urethane	H_2O TEA	Almost perfect surface due to thick epoxy layers. Over weight.
J-48-1	Epon 872 40 g	Same	Bonded to Nylon as in 1	Urethane 30 g	H_2O TEA	Show through from flutes. No wrinkles.
J-73-1	Epon 828 11.1 versamide 125 18.9	Nylon coated with epoxies	Bonded as in 1st	Urethane 30 g then 20 g	H_2O & TEA introduced at 3×10^{-5} mm Hg. H_2O 50 g TEA 5 g	Nylon had a seam across the center. On curing the seam did not show through. Recoated with urethane after 20 min. vac. desiccation at 200 μ. Good surface.
J-62-1	Epon 820 12 g versamide 125 28 g	Same	Bonded to nylon as in 1st	Urethane	H_2O 15 g TEA 5 g at 5×10^{-5} mm Hg	Flutes not fully inflated. 9" Hg pressure in collector.
J-76-2	Epon 820 12 g Versamide 125 18	Same	Same used to bond	Urethane 35 g then recoated	H_2O 50 g TEA 5 g at 3×10^{-5} mm Hg	9" Hg good surface & good cure.

* Epoxy formulations contained 0.3% PC 1344

TABLE 25.   VACUUM CURED 8 INCH SOLAR COLLECTOR

Exp. No.	Cushion and Structural Backing Materials			Resin System	Curing Agent		Results and Remarks
	1st layer	2nd layer	3rd layer				
R-50-1	Epon 872 30 g Epon 828 3 g	Same	Bonding to nylon; Same as 1	Urethane 40 g	H$_2$O TEA	40 g 4 g	Good surface. 8" Hg inside cover film.
R-52-1	Epon 828 32.5 g Versamide 125 17.5 g	Same	Bond to nylon; same as 1	Urethane 40 g	H$_2$O TEA	40 g 4 g	Fair surface. No show-through from backing 8" Hg.
R-55-1	Epon 828 32.5 g Versamide 17.5 g	Bonded with same as 1; wrinkles in film from nylon.		Urethane 40 g with 0.5% DMLA	H$_2$O TEA	40 g 4 g	Few wrinkles. 9.5" Hg between cover film & reflective surface.

TABLE 25.   VACUUM CURED 8 INCH SOLAR COLLECTOR   CONTINUED

a. Bench Cures

Table 26 describes six bench cured solar collectors. These experiments were performed to develop techniques of fabrication and cure and to test effectiveness of the alcohol emulsion bonding properties. Fiberglass strands referred to in the table are resin soaked glass roving to serve as a torus for added rigidity. These experiments showed scale effects on the "show-through" problem and the amount of rigidity required in the structural material.

b. Plasticizer boil-off system

Five 2 ft. collectors were cured in a vacuum by means of plasticizer boil-off of ADM's acrylic resin. The materials used to fabricate these collectors were as follows:

1. Acrylic Resin

2. Uncut nylon velvet with 5/8" pile between the faces

3. Epons 872-X-75 and 828

4. 3 mil aluminized Mylar

A thin coat of epoxy was brushed on the Mylar side of the film which had been placed in a set of rings and blown to a bubble. The nylon structural material was pre-formed by placing it over a polyethylene film coated with the uncured epoxy. This was also conducted on a set of rings with the polyethylene film pressurized to a bubble. After the pre-forming resin was cured, the coated nylon was bonded to the coated aluminized Mylar with still another layer of epoxy. The nylon was then impregnated with the acrylic resin and placed in a five foot diameter vacuum chamber for about 2 hours. Those epoxy mixtures yielded good reflective surfaces but were too rigid for packaging. The collectors weighed about 1 lb./ft.^{2}, mainly because the uncut nylon pile material was very heavy. Table 27 outlines the work done on acrylic cured solar collectors.

The work on acrylic resins was discontinued at this point because of excessive weight and insufficient cure-strengths. However, the experiments yielded much valuable information on fabrication and rigidizing techniques.

c. Vapor Phase Catalysis

A series of 2 ft. concentrators were fabricated and cured in a manner very similar to the final design described for the 8 inch models. Table 28 describes those experiments. Various epoxy combinations were tested in searching for a cushion which would prevent show-through and yet be flexible enough for packaging. A satisfactory bond was obtained between the Mylar and the flexible epoxies, Versamide 125 and Epon 872-X-75, even after blending in some rigid epoxy resin. The use of the polyvinyl acetate emulsion, N-42-1 was discontinued because of this fact.

TABLE 26. BENCH CURED 2 FOOT SOLAR COLLECTORS

Exp. No.	Cushion and Structural Backing Materials			Resin System	Curing Agent	Results and Remarks
	1st layer	2nd layer	3rd layer			
4-18-I	Epon 828 Epon T-1	Epon 828 Tri-PP 5% Epon T-1	Wimpf. Nylon Pre-formed	Epon 815	Epon T-1	Results: no bond Mylar peeled off.
4-22-I	N-42-1 emulsion	Epon 828 Tri-PP 5% Epon T-1	Wimpf. Nylon Pre-formed	Epon 815 Tri-PP	Epon T-1	Results: too much heat generated during curing, air bubbles and show-through. Good bond.
4-23-I	N-42-1 emulsion	Eponal 30	Wimpf. nylon pre-formed	Epon 815 Tri-PP	Epon T-1	Results: Show-through, wrinkles and weak backing.
4-24-I	N-42-1 emulsion	Epon 828 Tri-PP Epon T-1 (2 coats of above)	Wimpf. nylon pre-formed	Epon 815 Tri-PP	Epon T-1	Results: No show-through, good bond. Imperfections in film.
4-25-II	N-42-1 emulsion	Fiberglass mat	Wimpf. nylon pre-formed	Epon 815 Tri-PP	Epon T-1	Results: Show-through, and bubbles from power failure and small pin hole in Mylar.

Exp. No.	Cushion and Structural Backing Materials			Resin System	Curing Agent	Results and Remarks
	1st layer	2nd layer	3rd layer			
4-26-I	N-42-1 emulsion	Epon 828 Tri-PP Epon T-1 (2 coats of above)	Wimpf. nylon pre-formed	ِon 815 ِri-PP	Epon T-1	Fiberglass strands around base. Results: No show-through, wrinkles from backing.
5-23-1	N-42-1 emulsion	Epon 828 & 815 mixed; Tri-PP Epon T-1	Wimpf. nylon pre-formed	Epon 828 & 815 mixed; Tri-PP	Epon T-1	Fiberglass strands around base. Results: Wrinkles from backing show-through from cushion coats of Epon.

TABLE 26. BENCH CURED 2 FOOT SOLAR COLLECTORS   CONTINUED

Exp. No.	Cushion and Structural Backing Materials			Resin System	Results and Remarks
	1st layer	2nd layer	3rd layer		
R-40-1	N-42-1 emulsion	Epon 820 Epon T-1 2% SR-82	Wimpf. nylon pre-formed	ADM acrylic	Good surface. Good cure.
R-43-1	Epon 872, 125, 828, 75 Agent U 20. Cured 5 hrs.	Bakelite 2795 150 g plus 0822 3 g	Nylon pre-formed with Bakelite epoxy.	Acrylic 600 g Mel. form. 24 SMA 120	Epoxy coated nylon did not bond to 2nd layer.
R-44-1	Epoxy parts 872 125 828 75 Agent U 20, overnight cure.	Nylon pre-formed with thin coat as in 1st	Bond with same as 1st layer.	Acrylic 600 g Mel. form. 24 SMA 120	Wrinkled from cured resin used to pre-form nylon. Good bond.
R-44-2	Epon 872 50 Epon 828 150 Agent U 38 3 hr. cure.	Same as 1st layer	Nylon pre-formed, & bonded same as in 1 & 2	Acrylic 600 g Mel. form. 24 SMA 120	Good surface probably caused by amount of rigid resin. Nylon was cut to relieve tension.
R-46-1	Epon 872 50 Epon 820 150 Agent U 38 2½ hr. cure.	Same as 1st layer.	Nylon pre-formed, & bonded same as in 1 & 2.	Acrylic 700 Mel. form. 28 SMA 140 thinned with acetone.	Not completely cured. More cuts in nylon. Some fish eyes and air bubble show-through.

TABLE 27. VACUUM CURED 2 FOOT SOLAR COLLECTORS

Exp. No.	Cushion and Structural Backing Materials			Resin System	Results and Remarks
	1st layer	2nd layer	3rd layer		
R-47-1	Epon 872 100 Epon 828 100 Agent U 30; Overnight cure.	Same as 1st	Nylon coated & bonded with Epon 872 125 g Epon 820 75 g	Acrylic 700 Mel. form. 28 SMA 140 thinned with acetone.	Cut like R-46. 1 6" Hg pressure not completely cured. Mylar pulled away in places because of air trapped.
J-45. 1	Epon 872 100 Epon 828 100 Agent U 30	Same as 1st	Nylon coated & bonded with Epon 872 125 g Epon 820 75 g	Acrylic 700 Mel. form. 28 SMA 140 thinned with acetone.	Excessive pressure broke the film. Experiment dis- continued.

TABLE 27.   VACUUM CURED 2 FOOT SOLAR COLLECTORS   CONTINUED

Exp. No.	Cushion and Structural Backing Materials			Resin System	Curing Agent	Results and Remarks
	1st layer	2nd layer	3rd layer			
R-48-1	Epon 872 100 g Epon 820 100 g Agent U 30 g	Same	Same; 4th coat used to bond nylon.	Urethane 700 g 0.5% DMA	40 g TEA 400 g H$_2$O total in 4 sources.	8" Hg between cover plate and film. Good cure.
R-54-1	Epon 828 130 g Versamide 125 70 g	Epon 828 104 g Versamide 125 56 g	Used to bond the nylon.	Urethane 300 g 0.5% DMA	H$_2$O 400 g TEA 40 g	6" Hg on film. Wrinkles & show-through from flutes. Good cure.
R-56-1	Epon 828 80 g Versa. 125 80 g; Hard to brush.	Used to bond nylon.		Urethane 300 g	H$_2$O 400 g TEA 40 g	3.2" Hg between cover plate & film. Good cure but wrinkled surface.
R-57-1	Epon 828 56 g Versamide 125 104 g	Used to bond nylon.		Urethane 100 g	H$_2$O 400 g TEA 40 g	3.2" Hg. Good cure; wrinkles.

TABLE 28. VACUUM CURED 2 FOOT SOLAR COLLECTORS

Exp. No.	Cushion and Structural Backing Materials			Resin System	Curing ... .nt	Results and Remarks
	1st layer	2nd layer	3rd layer			
R-68-2	Epon 872 160 g Agent U 7.0 g Used to bond nylon.	Very flexible		Urethane 500 g	H_2O 400 g TEA 40 g Used 117 g H_2O & TEA.	1 mil Mylar. 4" Hg; poor surface. Very wrinkled.
R-63-1	Epon 828 56 g Versamide 125 104 g	Same	Same; 4th coat used to bond nylon.	Urethane 150 g, then 100 g.	H_2O 400 g TEA 40 g Used 120 g H_2O & TEA.	Done at Wright Field. Temp. variation from -70° to $+70^\circ F$. Cured only in warm zones.

TABLE 28. VACUUM CURED 2 FOOT SOLAR COLLECTORS   CONTINUED

ee coats of Epon 872-X-75 applied to the Mylar resulted in a very
flexible film which was well suited for packaging. The addition of up to 15%
Epon 828, a rigid resin, seemed to decrease the effects of fabric show-through
without seriously impairing the flexibility of the film. It was noted that an
orange peel effect became apparent only after bonding the fluted nylon structural
material to the epoxy film. The greater the number of cushion layers, or the
more rigid the epoxy mixture, the less show-through ocurred. All of these
collectors except R-63-1 were cured in $1\frac{1}{2}$ to 2 hours in a 5 foot diameter vacuum
chamber at a pressure of 1.5 to 2 mm Hg. Pressure between the cover film and the
reflective surface was provided as discussed in the section about 8 inch collector
models. Figure 19 shows the experimental set-up installed in the vacuum chamber.

The pre-formed nylon was sewn together around the periphery to cause inflation
of the urethane impregnated fabric when water vapor pressure was introduced
between the faces of the material. In all cases, good inflation of the fluted
material resulted when water and triethyl amine vapors were valved into the
flutes starting at initiation of pump down. Figure 20 shows the cured structural
material on the 2 ft. model. Experiment R-63-1 was performed at Wright Field
in a 3 ft. diameter x 5 ft. long vacuum facility with cold walls installed. This
collector was first impregnated with urethane and desiccated for 20 minutes to
about 1 mm Hg. The fabric was then impregnated with an additional urethane coating,
reinstalled in the chamber, and an attempt was made to cure the structure. Water
and TEA were released from outside at 5.8×10^{-5} mm Hg. The pumping capacity of
the chamber was not sufficient to hold the low pressure after release of the
catalyst vapors. Thermocouples and a recording device indicated the temperature
on the structural material varied from -70°F close to the rim to 75°F near the
middle on the back side. The flutes inflated only in the center portion which
was warmed intermittently by means of a heat lamp. Resin in the -70°F zone did
not cure.

These experiments with 2 ft. models revealed that the system selected for
final design, fabrication, and rigidization was operable and produced satisfactory
solar collector models. Figure 21 shows a vacuum cured 2 ft. solar collector model.

3.   5 Ft. Diameter Solar Collectors

Two 5 foot diameter solar collectors were prepared at Viron and made ready
for impregnation and vacuum cure at Wright Field. Two coats of flexible epoxy
were spread over a preformed 3 mil aluminized Mylar film. Another coat of this
mixture served as the bonding layer for the nylon structural material.

The composite was very flexible and easily rolled into about a 4 inch diameter
tubular shape, Figure 22. At Wright Field, on October 9, 1963, the nylon struct-
ural material was impregnated with $3\frac{1}{2}$ lb. of polyurethane resin and placed in the
high altitude vacuum chamber as shown in Figure 23. Water and triethylamine
vapors were piped from outside the chamber into four distribution points in the
backing material. For 2 hours the environmental pressure was kept at 1 mm Hg.
Thermocouples, imbedded in the structural material near the center and outer edge,
indicated temperatures of about 120°F and 80°F respectively as a result of flood-
lights focused on the backing material. Good inflation of the flutes was obtained
and the reflective surface was fair. The finished product is shown in Figures 24,
25, and 26.

On October 10, 1963 another five foot solar collector was cured in the same
manner with similar results.

SECTION 7

CONCLUSIONS

A. The feasibility of rigidizing expanuable honeycomb material by vapor catalysis
has been demonstrated. The two resin systems found to be most successful were
the urethane and epoxy resins. The urethanes, because of their reactivity at
moderate temperatures and their short cure time (approximately 1 to 2 hours at
room temperature) under laboratory conditions, were chosen as prime candidate
resin for this contract. Sufficient physical strengths have been achieved with
urethane prepolymers cured with a catalyst system of water-triethyl amine vapor.
Resin to glass weight ratio of between 30-40% provides maximum efficiency.

B. The commercial epoxy resins have been screened and the Novalac epoxy polymer
chosen as the most adaptable for use. In comparison to urethanes, the one serious
limitation to the epoxy is the long cure time necessary (16 hr.) under vacuum
conditions. The high degree of tackiness remains another limitation. Conversely,
the improved flexural and tensile strengths of the epoxy vapor cured laminate is
superior to the urethane impregnated laminates. Resin to glass weight ratio of
40% is effective for the epoxy system.

C. The feasibility of rigidizing expandable honeycomb material by plasticizer
boil-off has been demonstrated. A rapid rigidization of impregnated glass fabric
is achieved when employing a 40% non-volatile 3-component system (acrylic, styrene-
maleic anhydride copolymer, and melamine resin) solvalyzed with acetone. The
polyacrylic resin contains 60% NV and is diluted with a xylene/butanol solvent
mixture. 20% by weight SMA (3000 molecular weight) copolymer is added as is 5%
by weight of melamine resin. The entire viscous mixture is further diluted to
workable viscosities by the addition of acetone. Removal of the solvents leaves
a rigidized substance of acceptable physical strengths.

D. The design, fabrication, and rigidization of an expandable, self-rigidizing
space shelter using sandwich type completely flexible structural material has
been shown feasible through the delivery of a 7 ft. diameter shelter rigidized
in a vacuum environment. Fine details learned in the development stage can be
listed as:

1. Inflation to keep the walls separated can be accomplished with excess pressure
relative to the environment.

2. Care must be exercised to seal all seams and other possible points of excess
vapor loss when curing a structure by vapor catalysis.

3. Plastic liners can be used to assist erection of the structure without excessive
impairment of vapor cure.

E. The design, fabrication, and rigidization of an expandable, self-rigidizing
solar energy concentrator using sandwich type completely flexible structural
material has been shown feasible through the delivery of a 5 ft. diameter collector

rigidized in a vacuum environment. More detailed findings in the development stages can be listed as:

1. A flexible layer of an organic polymeric resin can be used to hide "show-through" of the structural material and to bond all components into a completed unit ready for erection and rigidization.

2. Having all parts, which go into the completed unit, pre-formed accurately to eliminate as much stress concentration as possible results in the most operable system for remote inflation and rigidization.

3. Vapor phase or plasticizer boil-off curing of resin impregnated structural material used to retain the shape of a solar collector has been shown feasible.

SECTION 8

RECOMMENDATIONS

A. The vapor cured epoxy system, because of its inherently stronger physical properties, should receive a continuing evaluation in such areas as:

1. Accelerator addition to speed reaction rates of cure.

2. Faster acting catalyst systems.

3. The synthesis of dormant, blocked catalyst which can be regenerated upon demand by gaseous materials.

4. The synthesis of modified epoxy systems, modified to give better physical properties and faster reaction rates.

B. The urethane system, chosen as prime resin candidate for AF contract 33(657)-10409, has a future in this type of application. Several recommendations are to be made which include the following:

1. Further synthesis be made to modify urethane prepolymers to obtain faster reacting prepolymers with increased physical strengths. The use of prepolymers with rigid chemical backbones introduced through the employment of aromatic or acyclic diols, polyols, and diisocyanates should create an increase in rigidity and physical strength.

2. Efforts should be made to obtain workable viscosities without the use of volatile solvalyzing components.

3. Methods to generate catalyst in situ through the employment of dormant, blocked catalyst systems should be explored.

4. Radical ure ine modifications are contemplated which would give indefinite shelf-life stability of urethane impregnates still remains a problem to date for extended time periods.

5. An attempt to find urethane reaction accelerators with shelf-life stability would open the way for faster rates of cure and a greater cross-linking index for the resin system.

C. The study of polyester resins for this vapor phase curing application should be examined closely. The synthesis and use of volatile peroxides or latent peroxides would offer many advantages to this system.

D. Within the plasticizer boil-off program, further effort should be devoted to the study of plasticized natural products such as protein, gelatin, or modifications of those. The inherent physical properties of the natural products make them attractive for architectural applications.

E. Further development of the materials to be used and the fabrication techniques is needed for the space shelter portion of the study. Specifically:

1. Develop an actual integrally woven flexible honeycomb material.

2. Vary the weave pattern of the material faces.

3. Further develop seaming and joining techniques.

4. Develop the capability to determine material porosity.

F. Further development of the materials to be used and the fabrication and rigidizing techniques for the solar collector study is needed. Specific areas where further study is needed are:

1. Development of a bonding, show-through absorbing, flexible layer to coat on the reflective surfaces.

2. Development of an optimum sandwich type configuration for the structural material.

3. Development of a catalyst container.

4. Development of a system for expanding the assembly to the desired shape.

5. Development of a canister for transportation of the collector into space.

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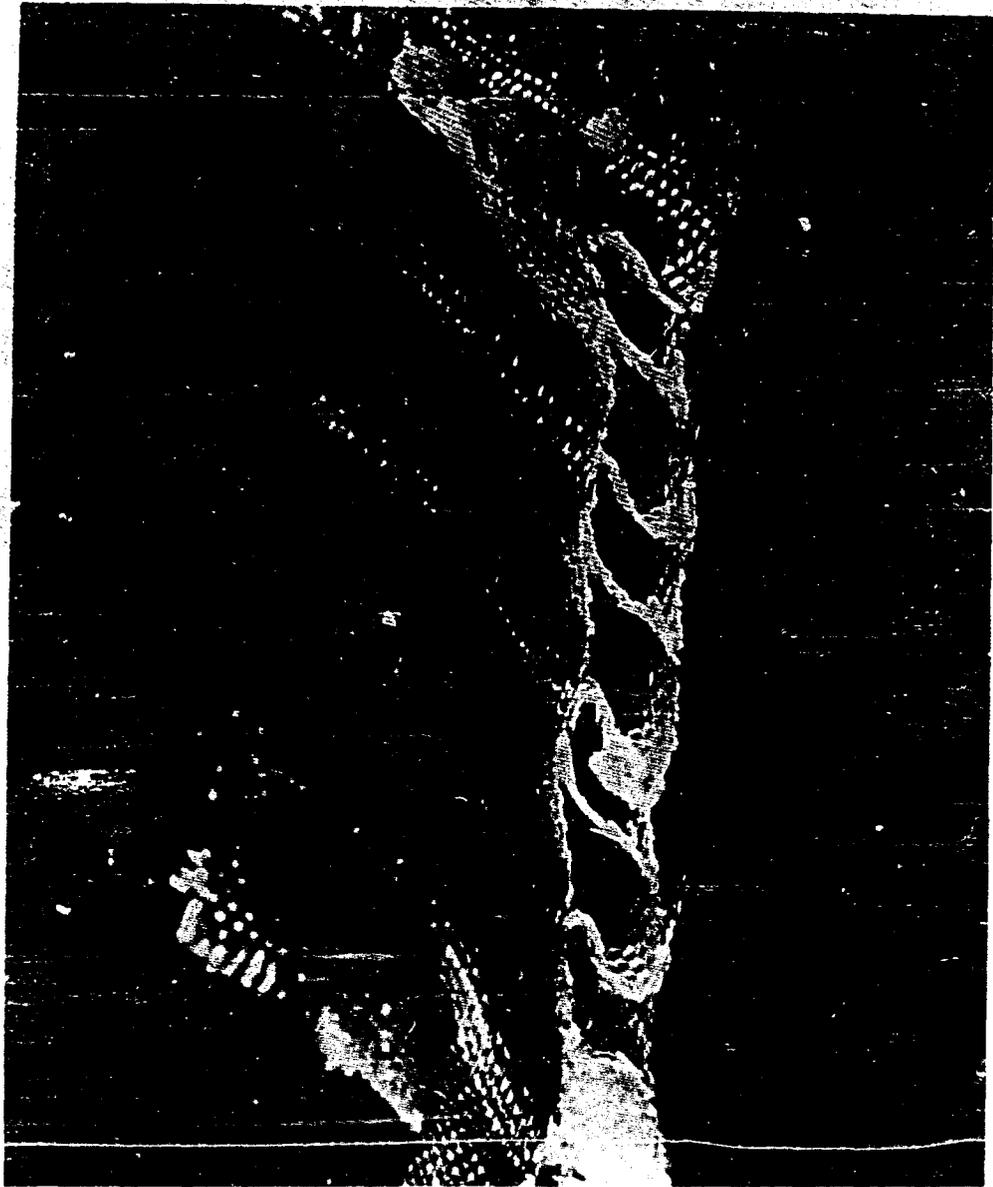
FIGURE 1. UNIMPREGNATED RAYPAN FLUTED MATERIAL

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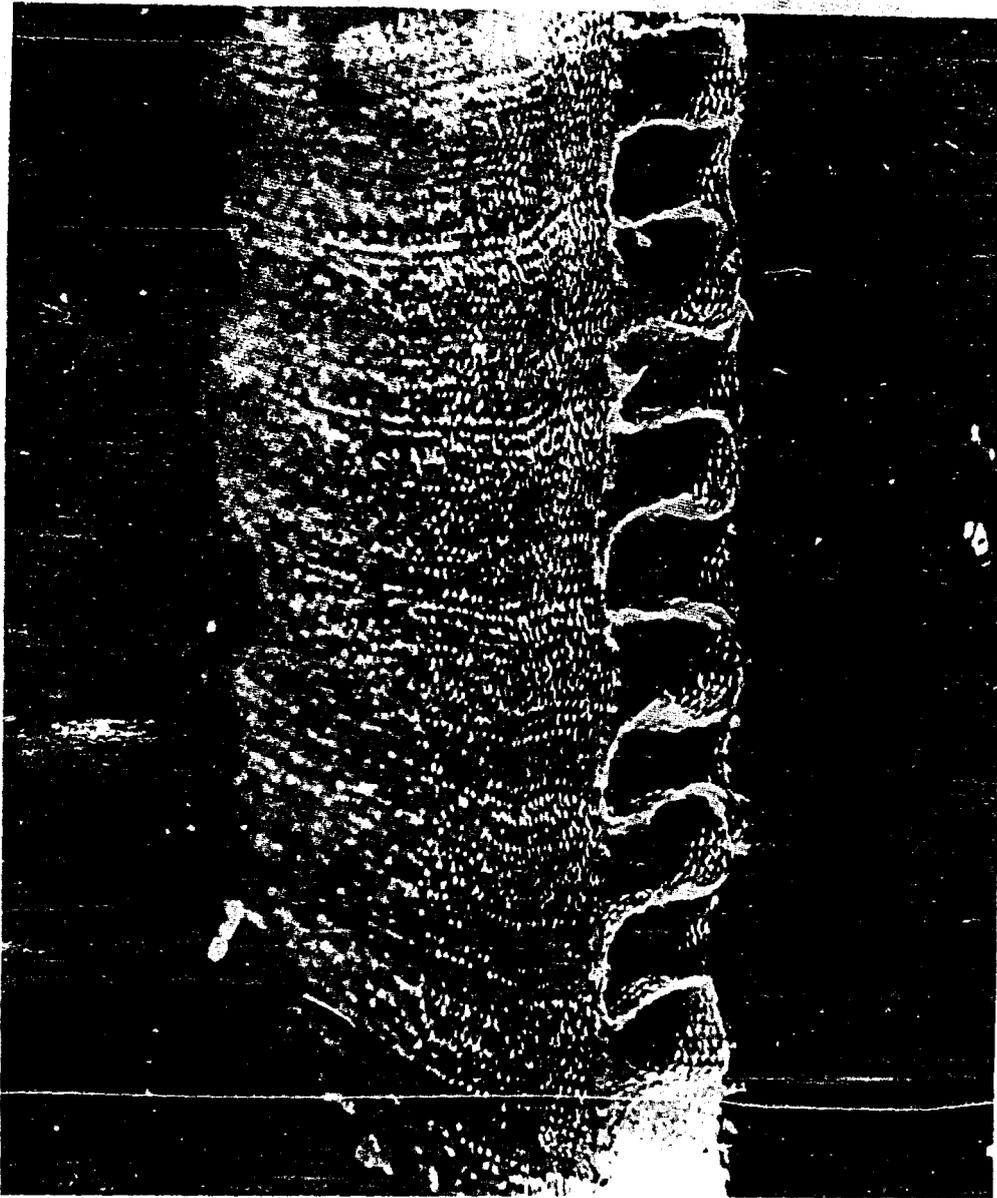
FIGURE 2. IMPREGNATED, EXPANDED, AND CURED RAYPAN FLUTED MATERIAL
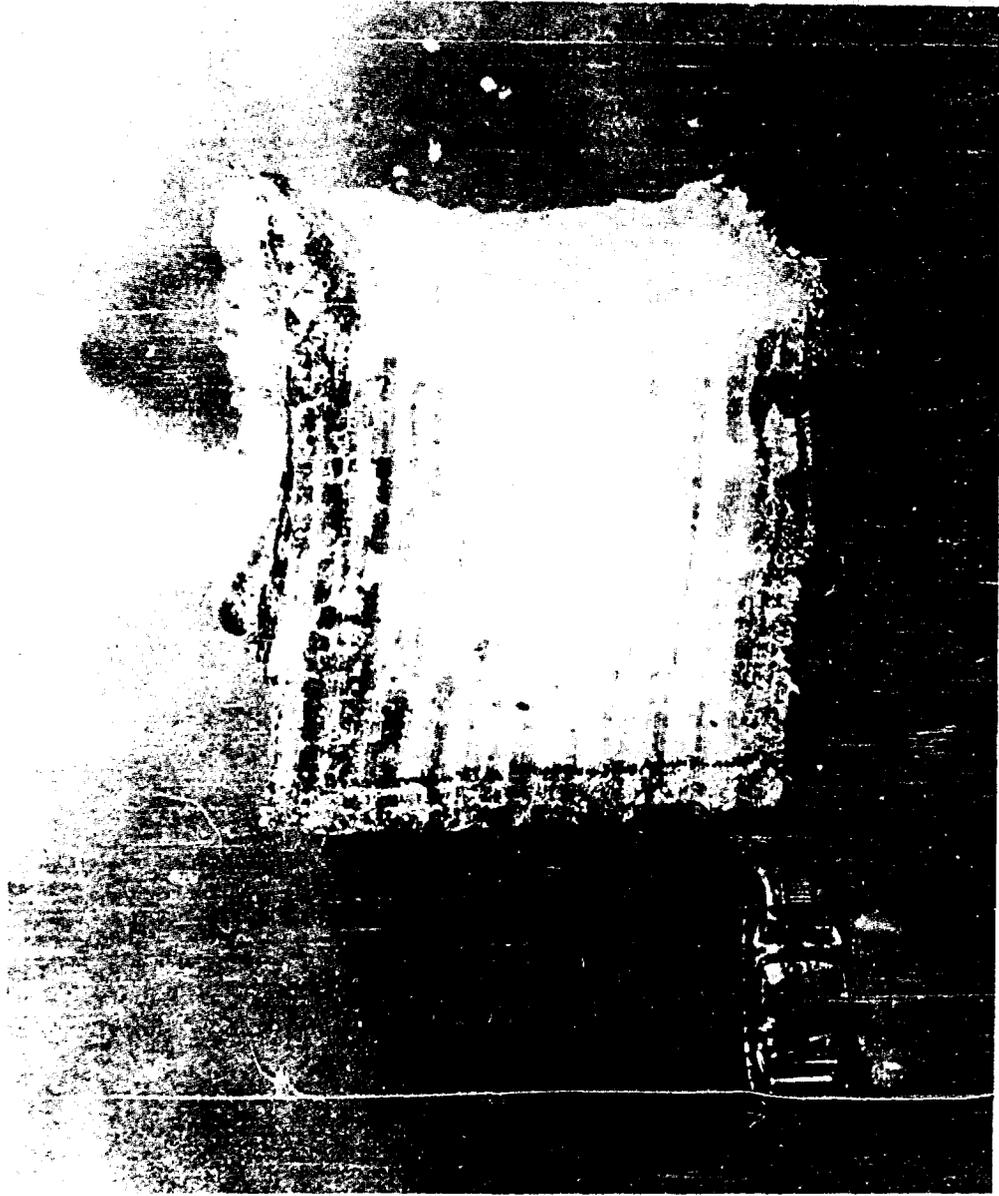
FIGURE 3. FIBERGLASS CUBE CURED IN A VACUUM WITH A URETHANE RESIN
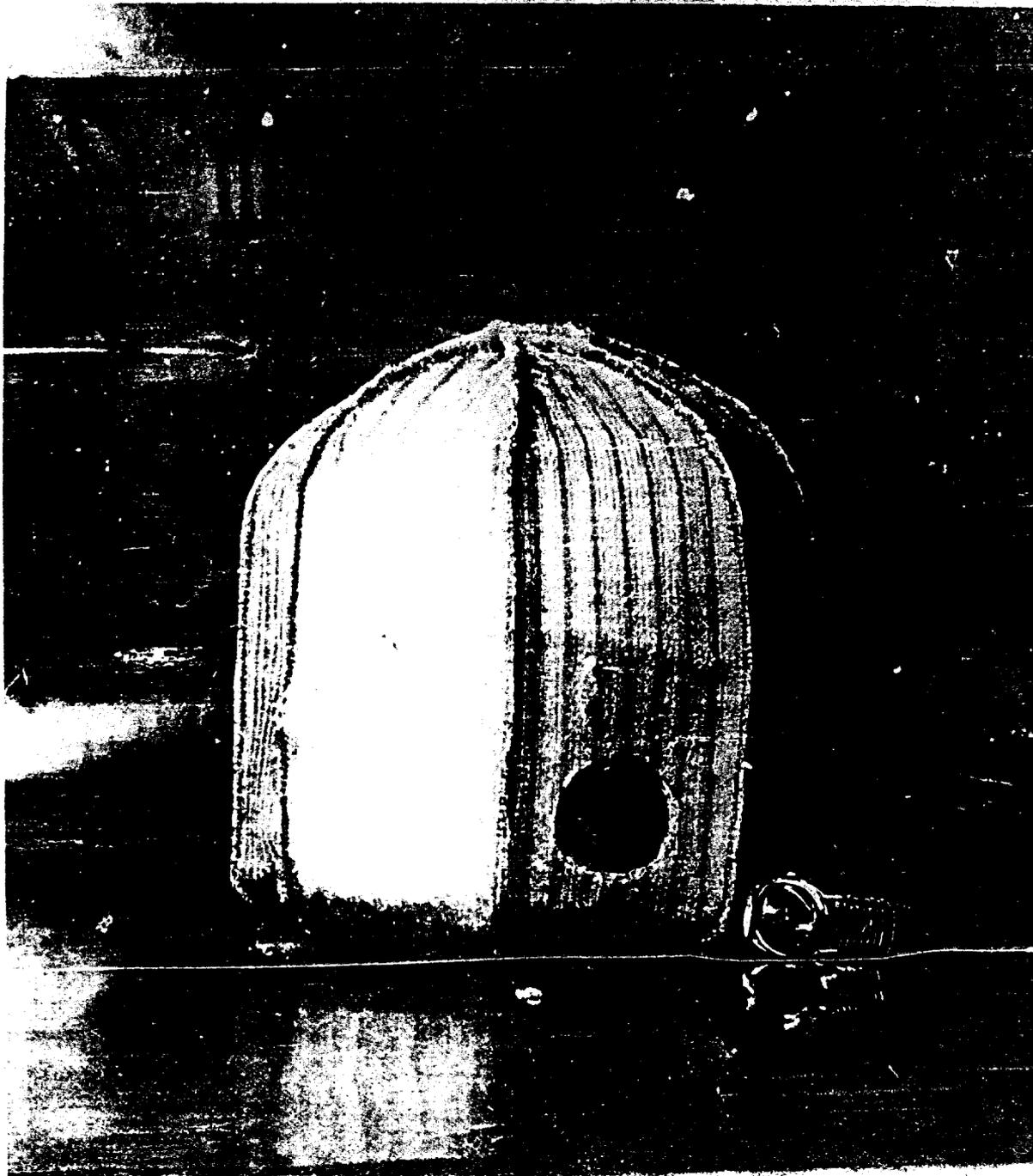
FIGURE 4. FIBERGLASS SHELTER MODEL, 1/10 SCALE, VAPOR CURED EPOXY
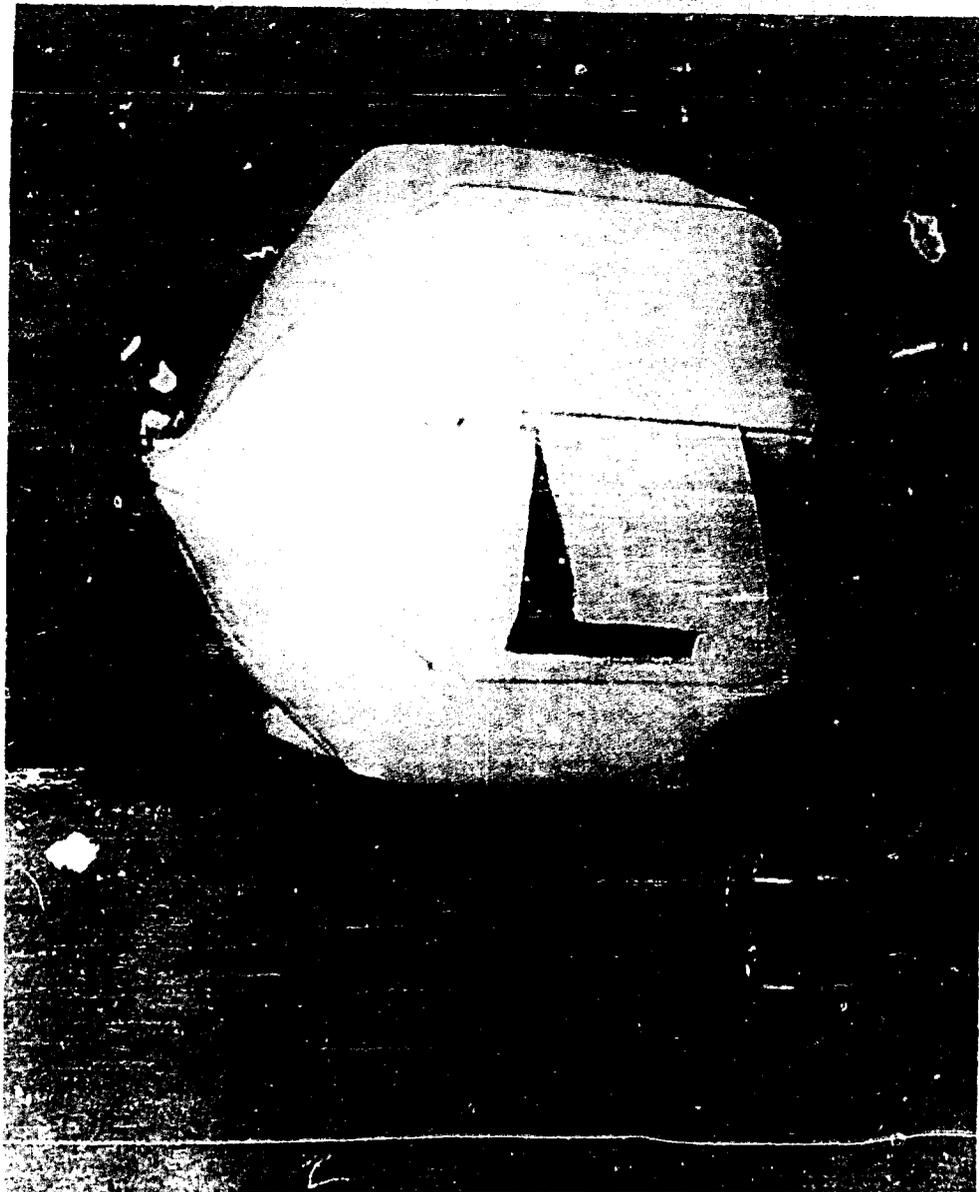
FIGURE 5. NYLON SHELTER MODEL, 1/10 SCALE VAPOR CURED EPOXY
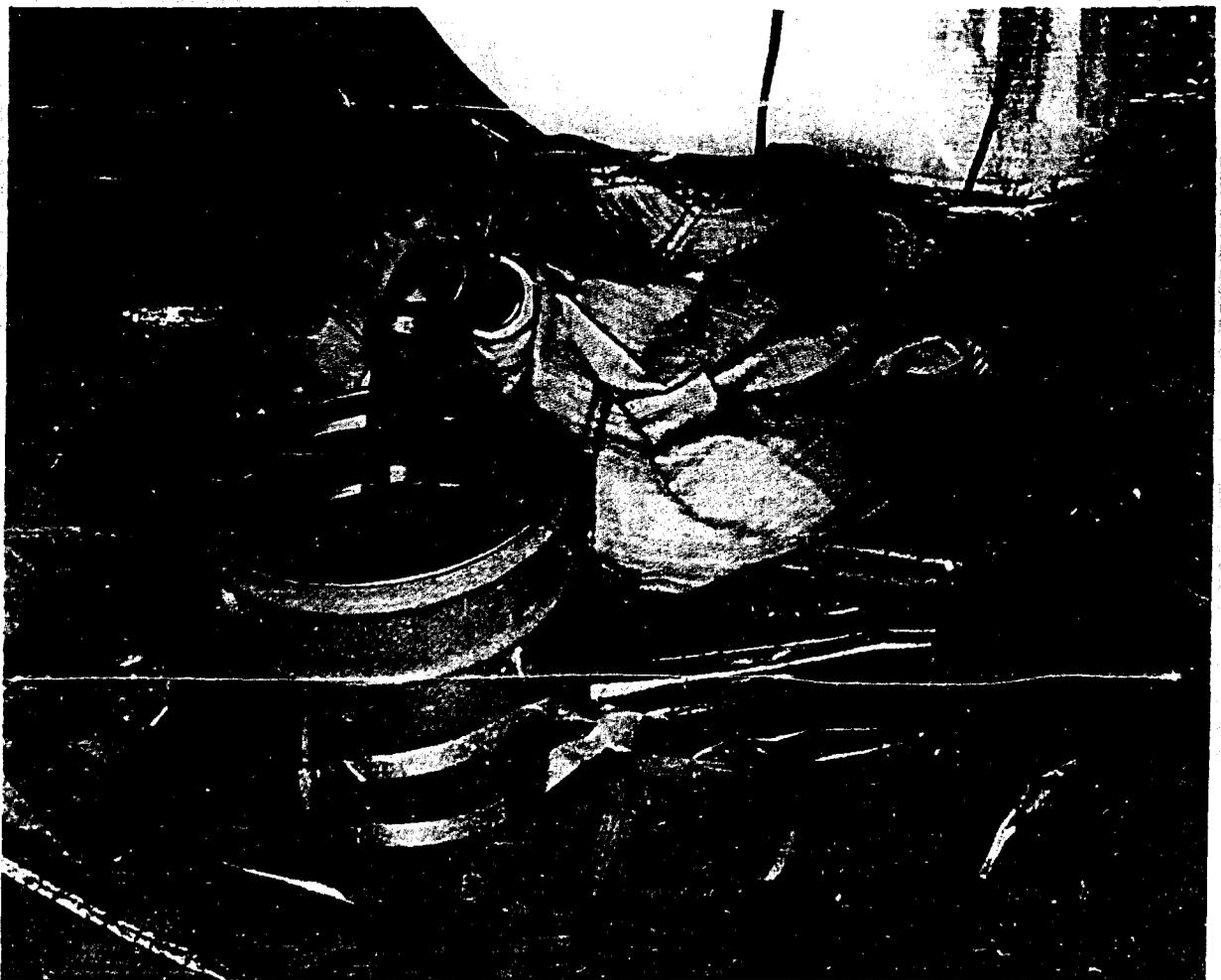
FIGURE 6. IMPREGNATED 1/2 SCALE SHELTER MODEL IN VACUUM CHAMBER
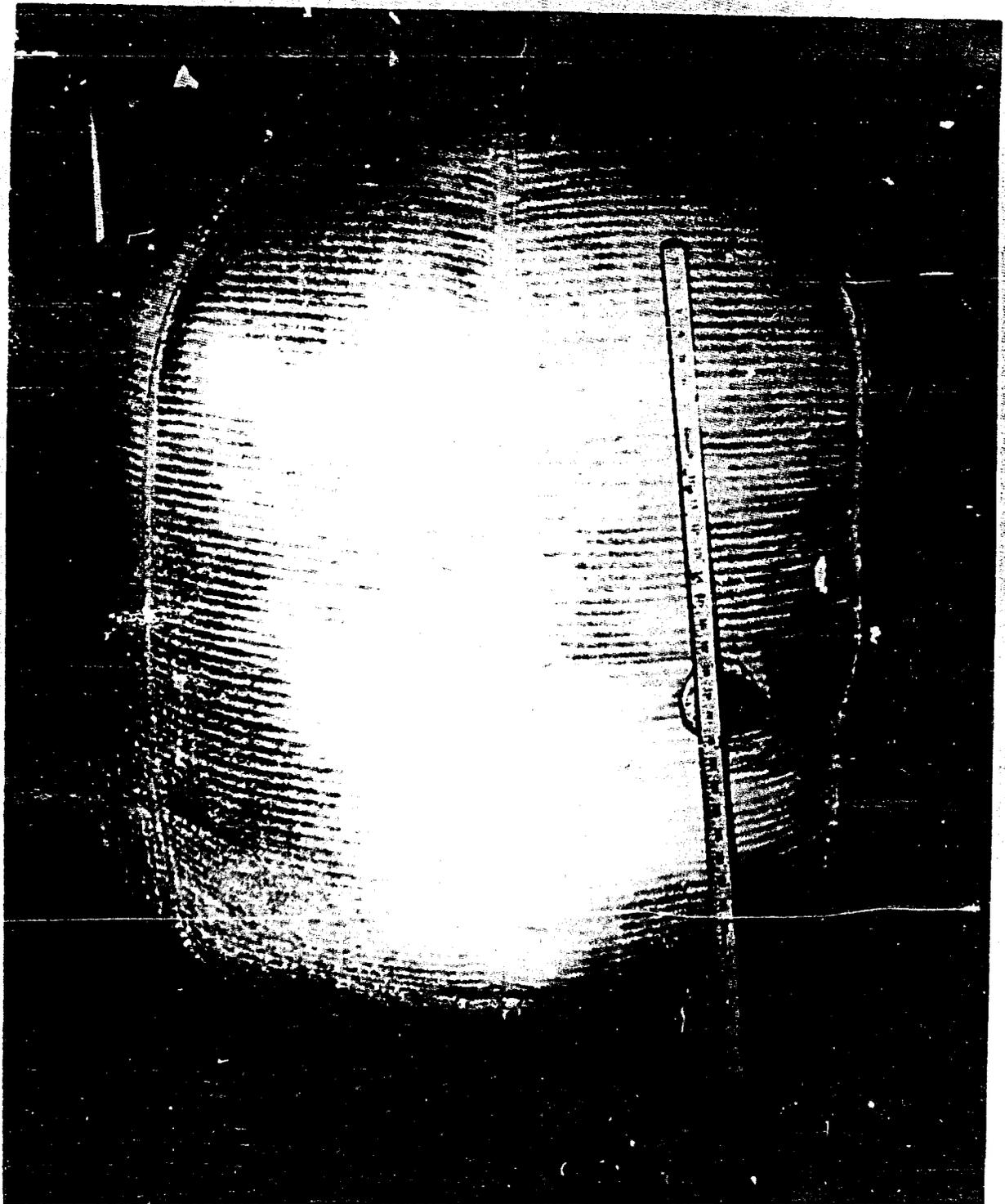
FIGURE 7. VACUUM CURED 1/2 SCALE SHELTER MODEL
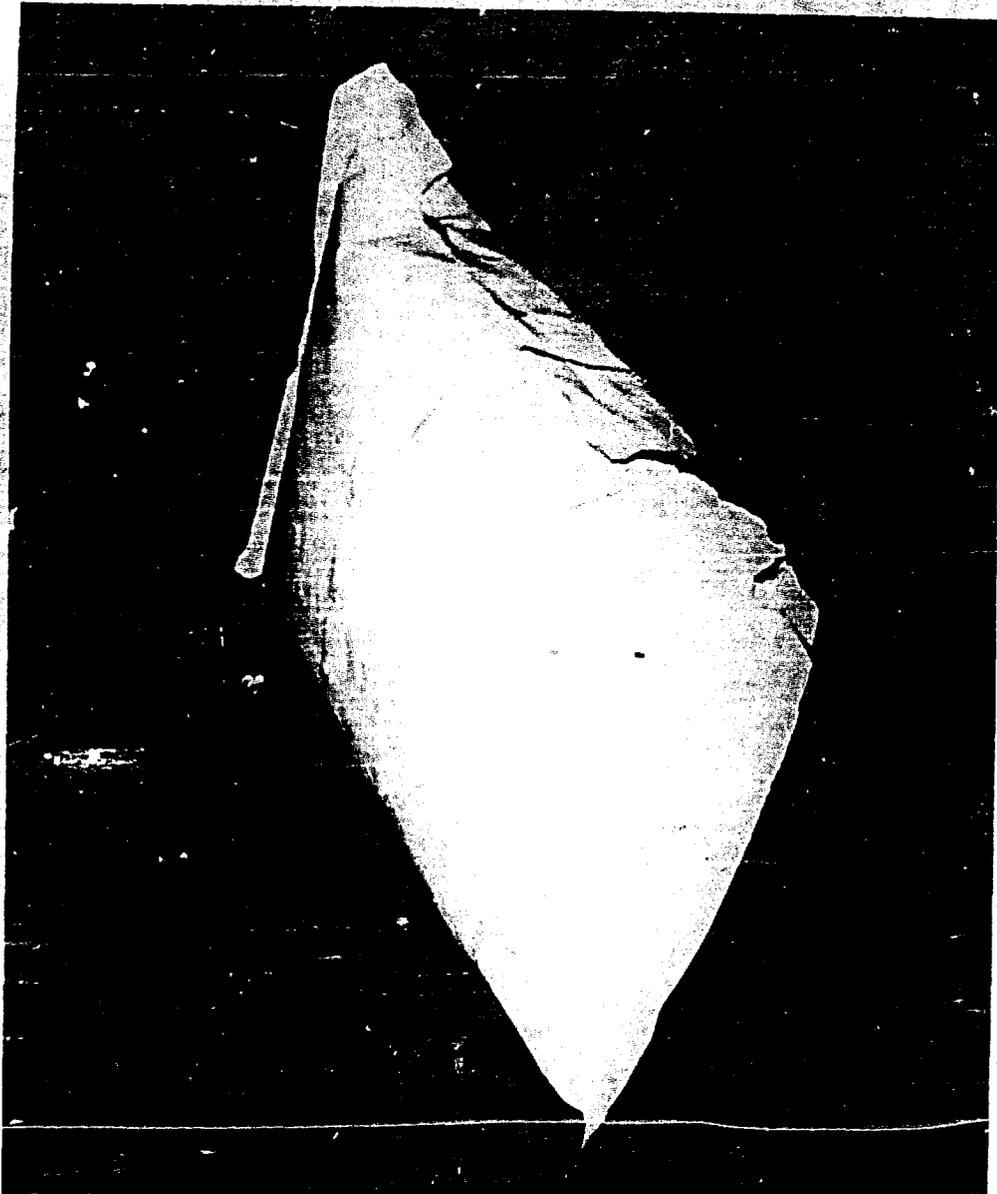
FIGURE 8.   IMPREGNATED AND PACKAGED 1/2 SCALE SHELTER MODEL
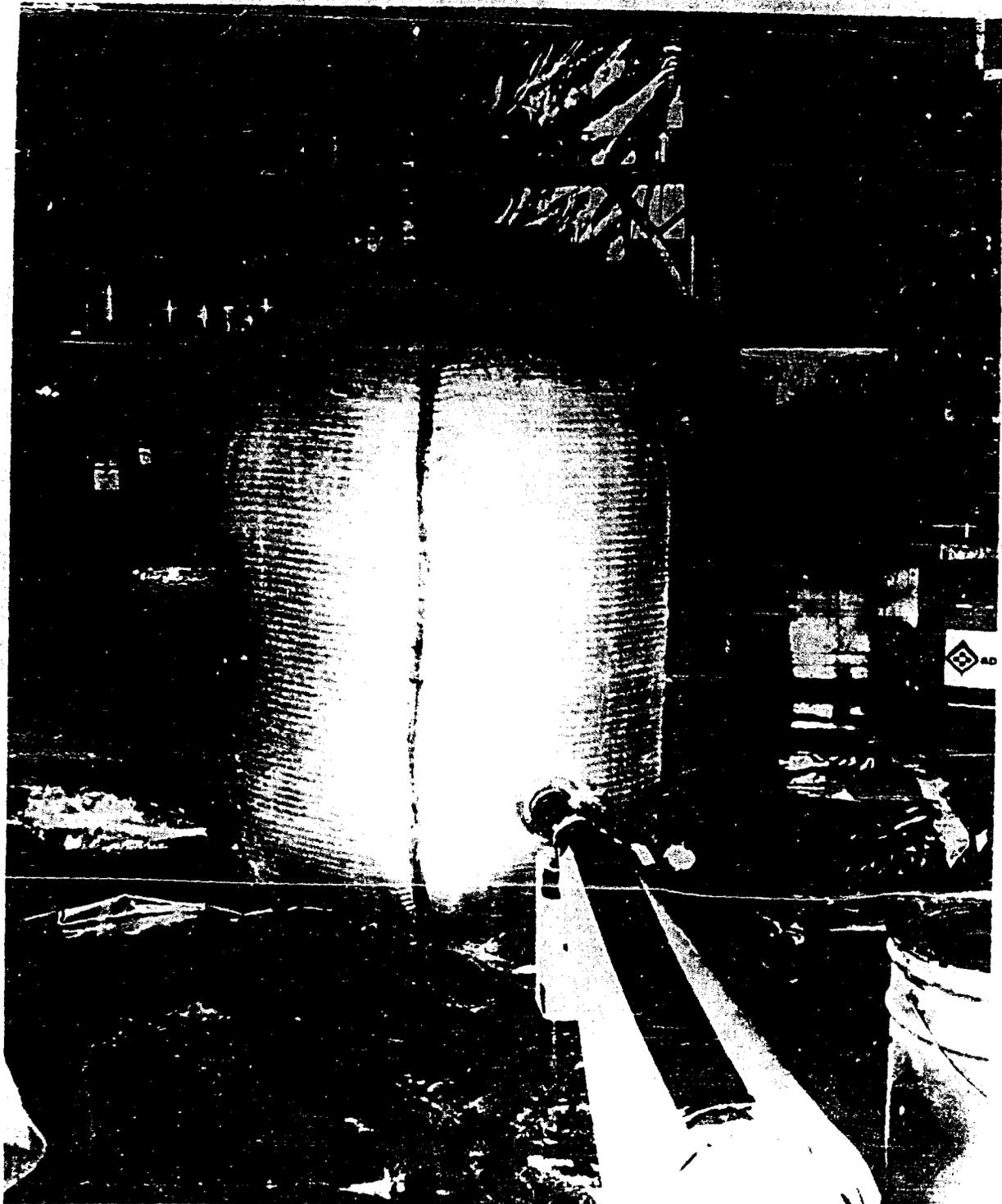
FIGURE 9. INFLATED 1/2 SCALE SHELTER MODEL
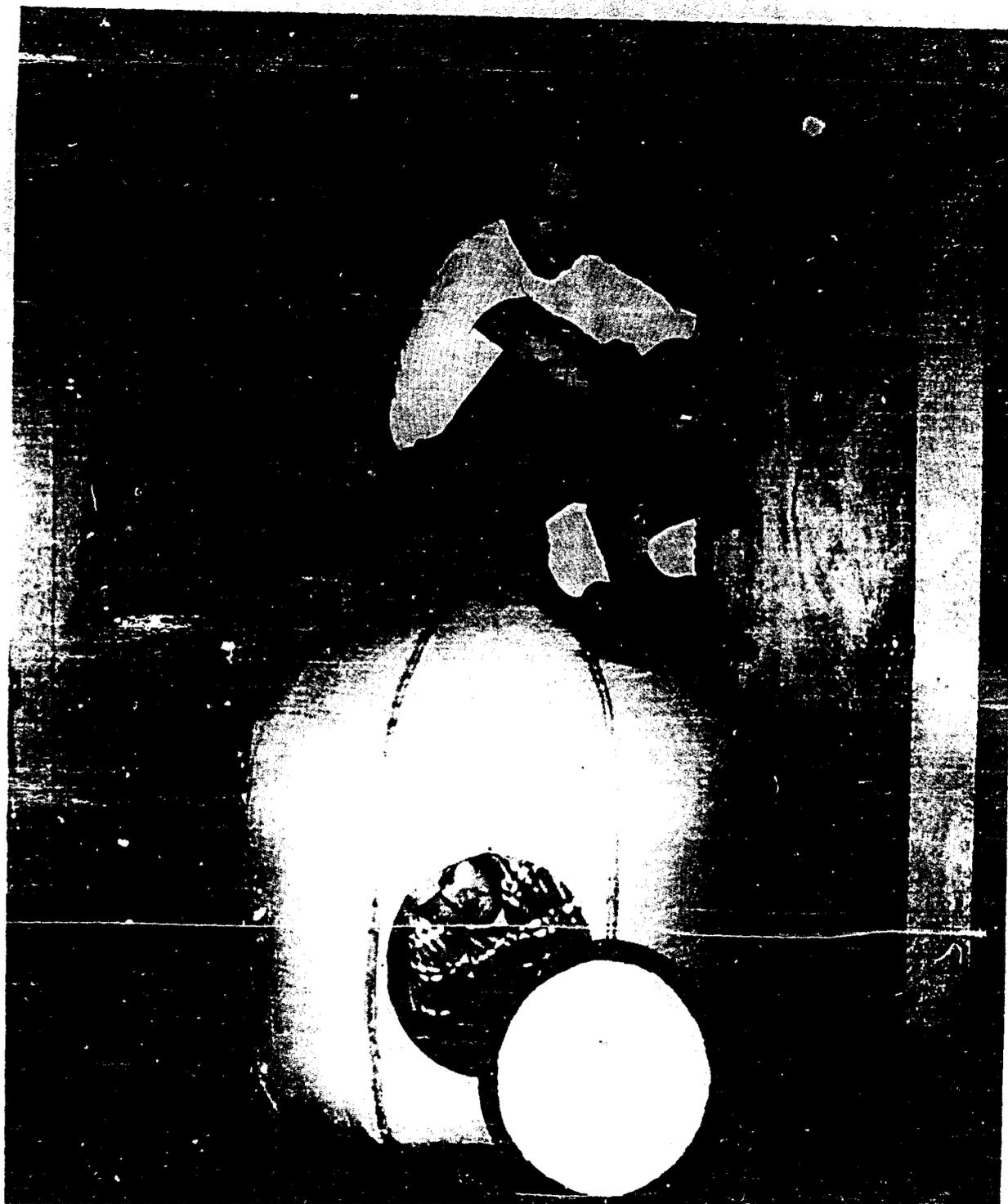
FIGURE 10. CURED 1/2 SCALE SHELTER MODEL

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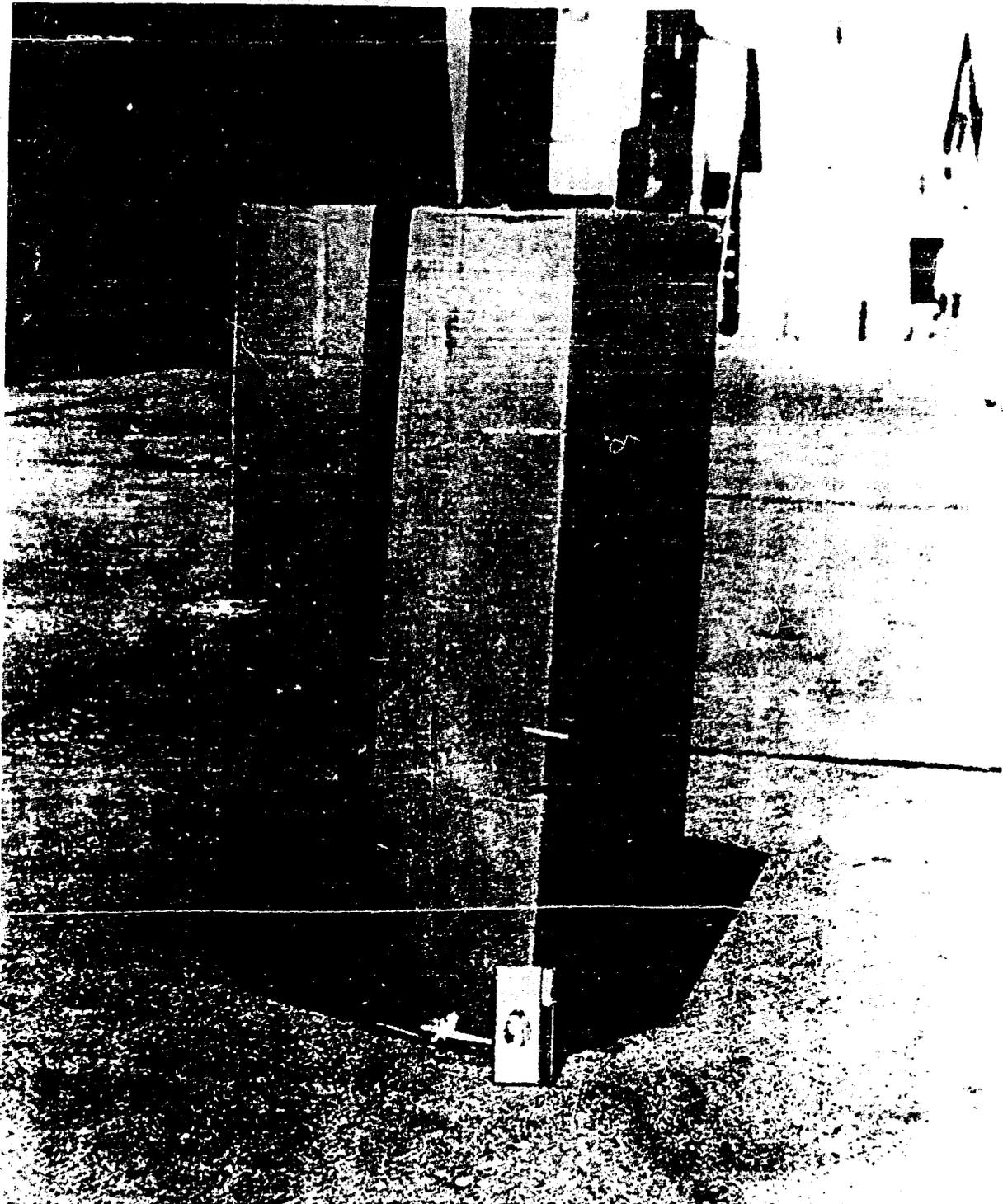
FIGURE 11. PACKAGED FULL SIZE SHELTER

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FIGURE 12. VACUUM IMPREGNATION OF FULL-SIZE SHELTER
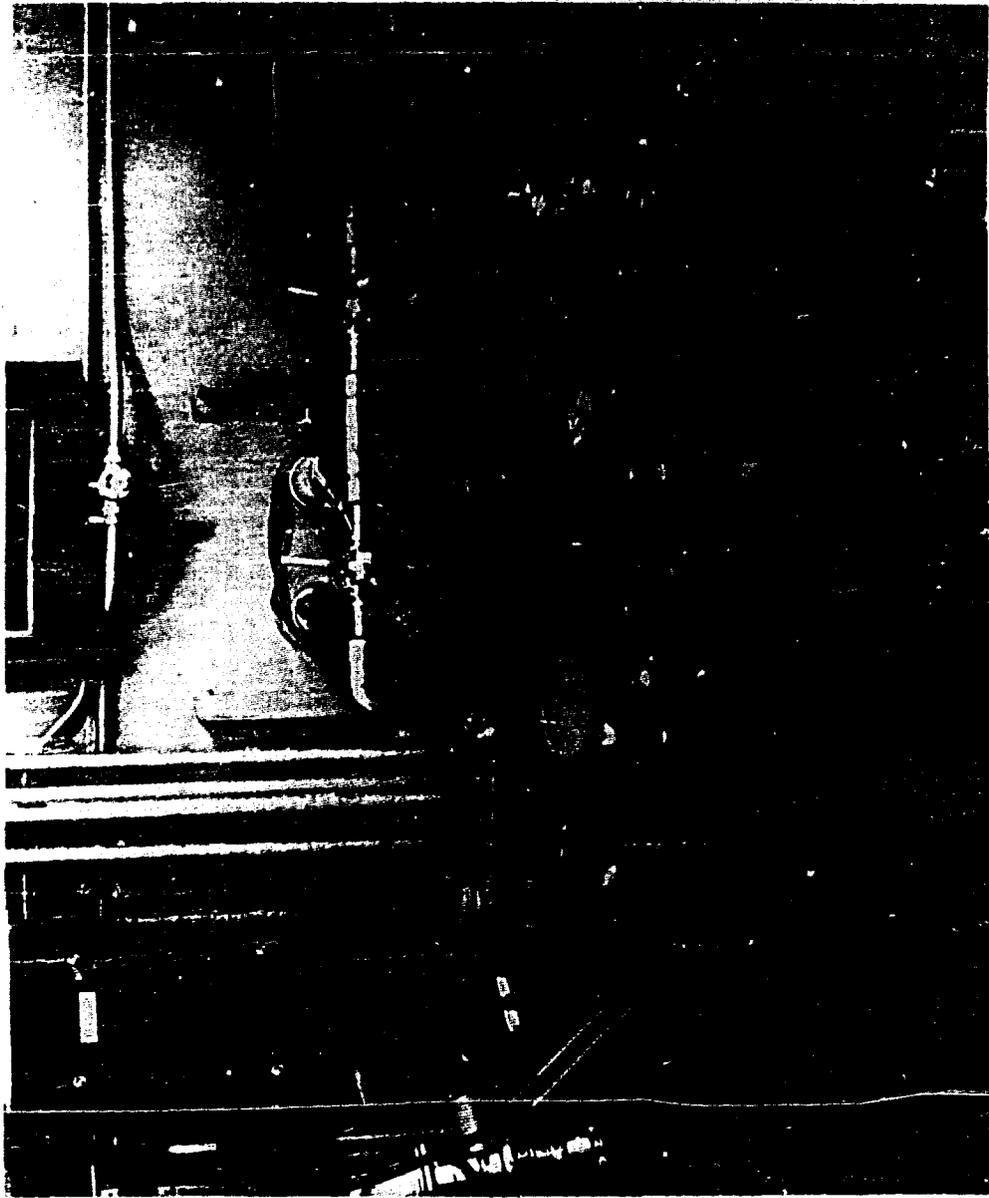
FIGURE 13. WATER SUPPLY SET-UP
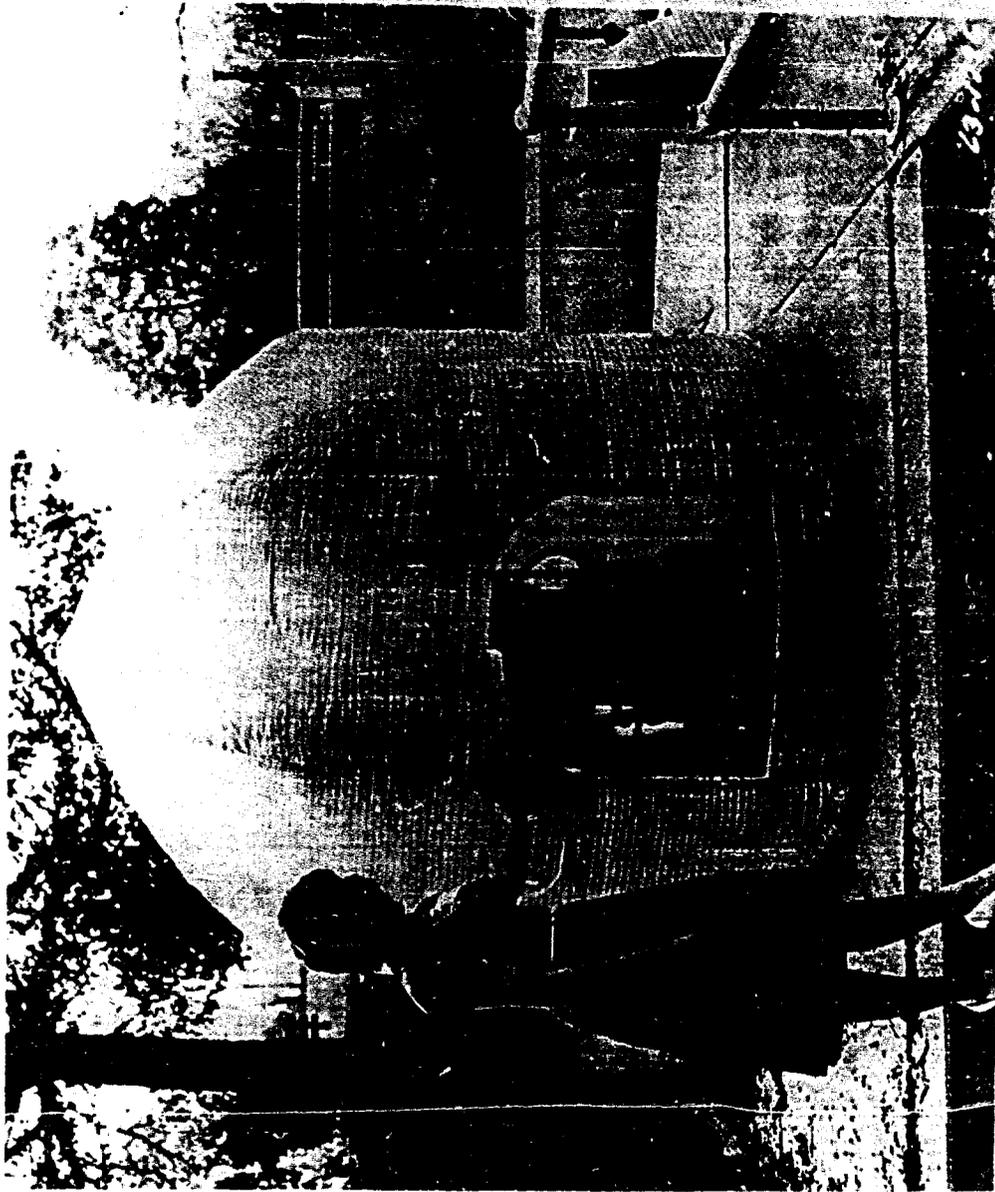
FIGURE 14. CURED FULL SIZE SHELTER
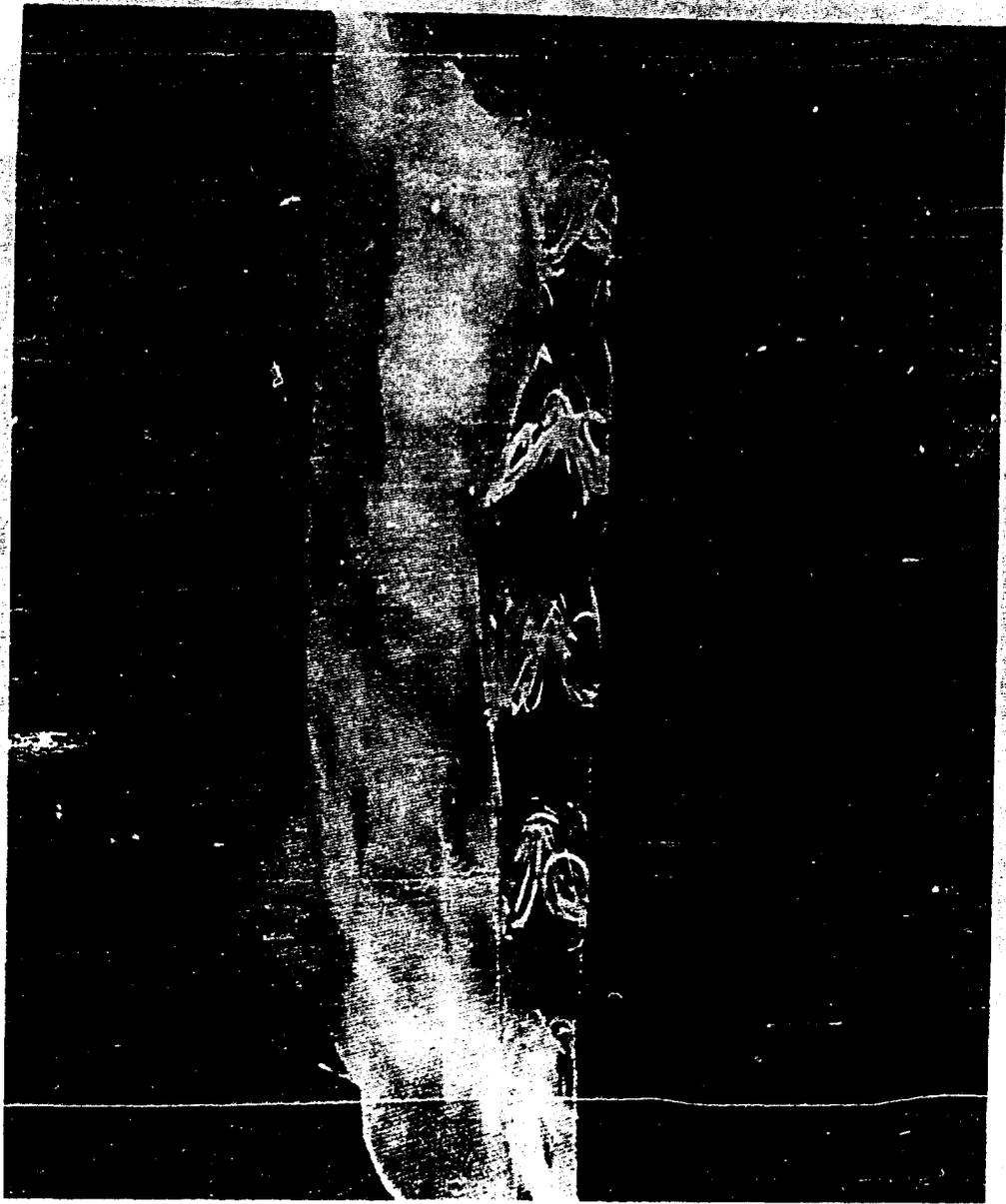
FIGURE 15. UNIMPREGNATED SOLAR COLLECTOR STRUCTURAL MATERIAL
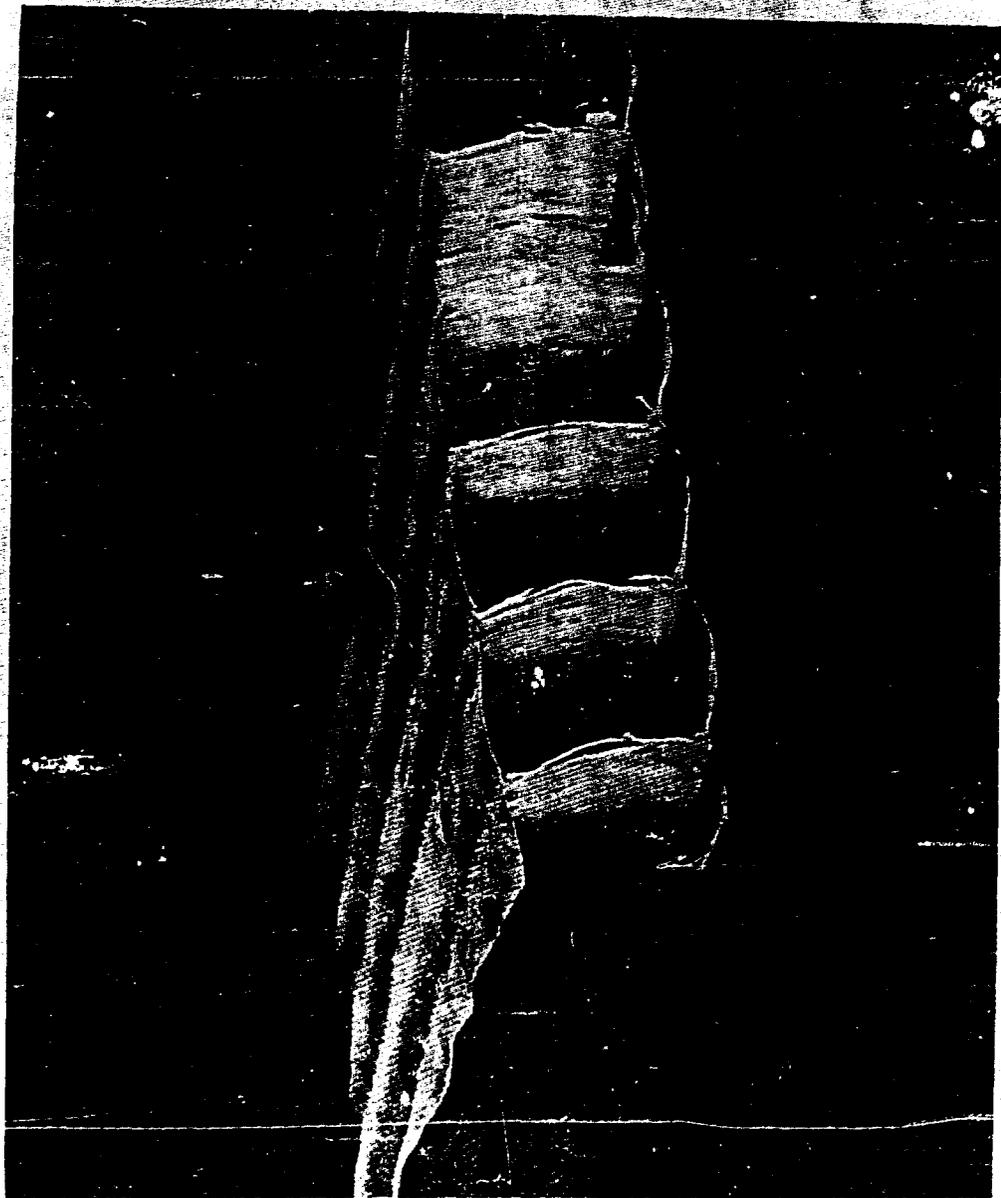
FIGURE 16. IMPREGNATED SOLAR COLLECTOR STRUCTURAL MATERIAL

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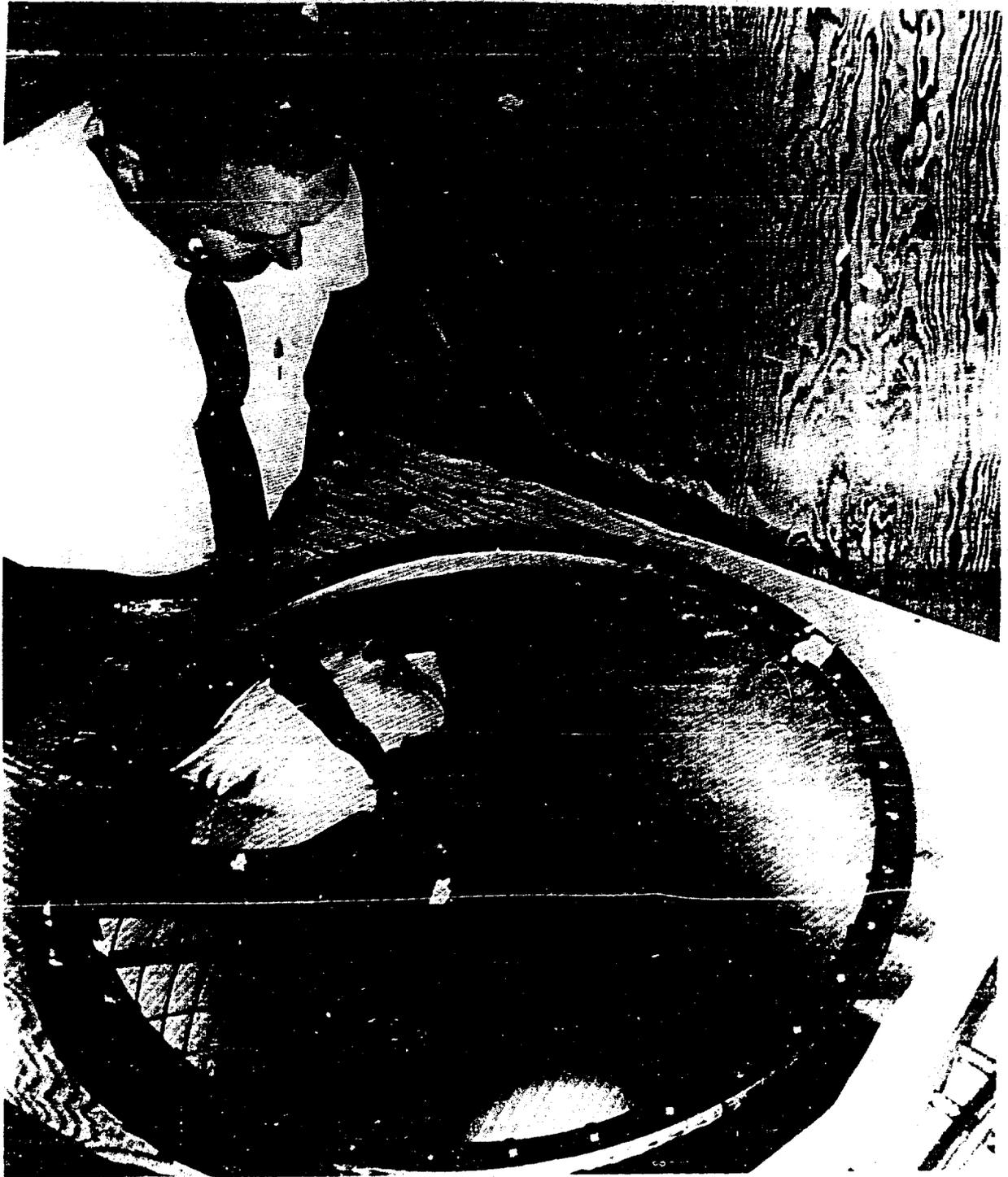
FIGURE 17. PREFORMED FILM HELD IN PLACE WITH METAL RINGS
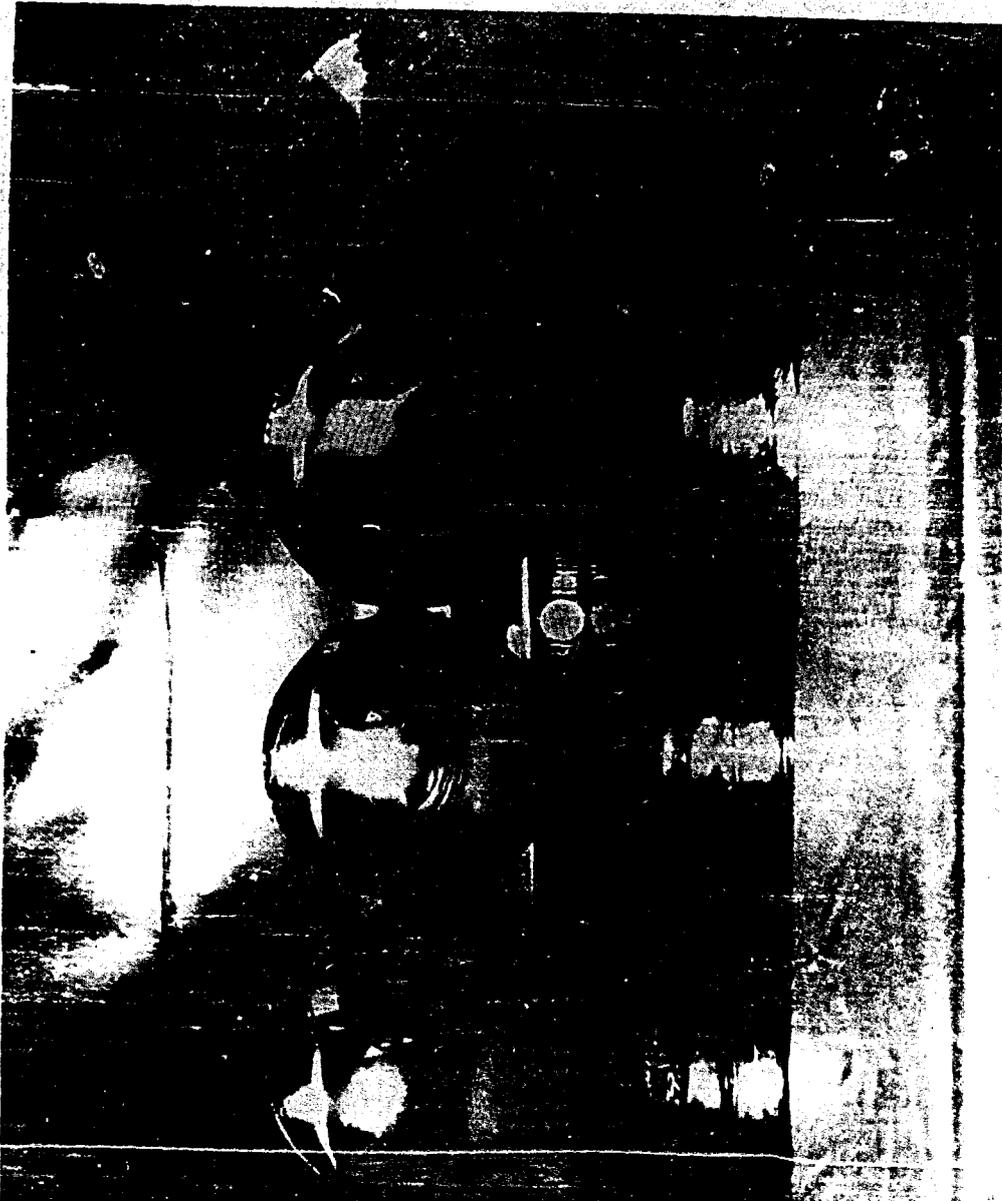
FIGURE 18. EARLY BENCH CURED 3" SOLAR COLLECTOR MODELS

FIGURE 19. 2 FT SOLAR COLLECTOR MODEL INSTALLED IN VACUUM CHAMBER
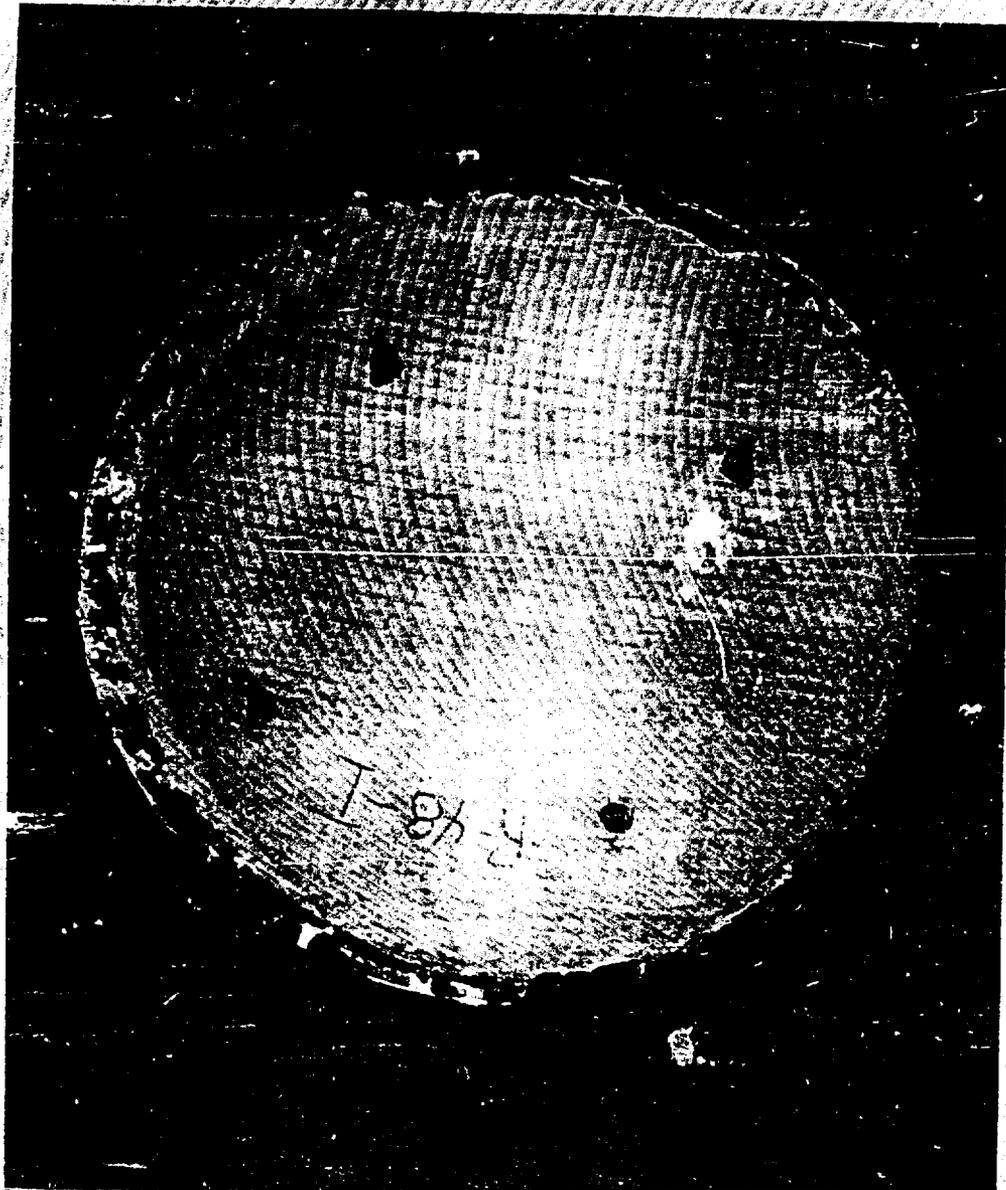
FIGURE 20. 2 FT SOLAR COLLECTOR MODEL CURED STRUCTUPAL MATERIAL

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FIGURE 21.   VACUUM CURED 2 FT SOLAR COLLECTOR MODEL
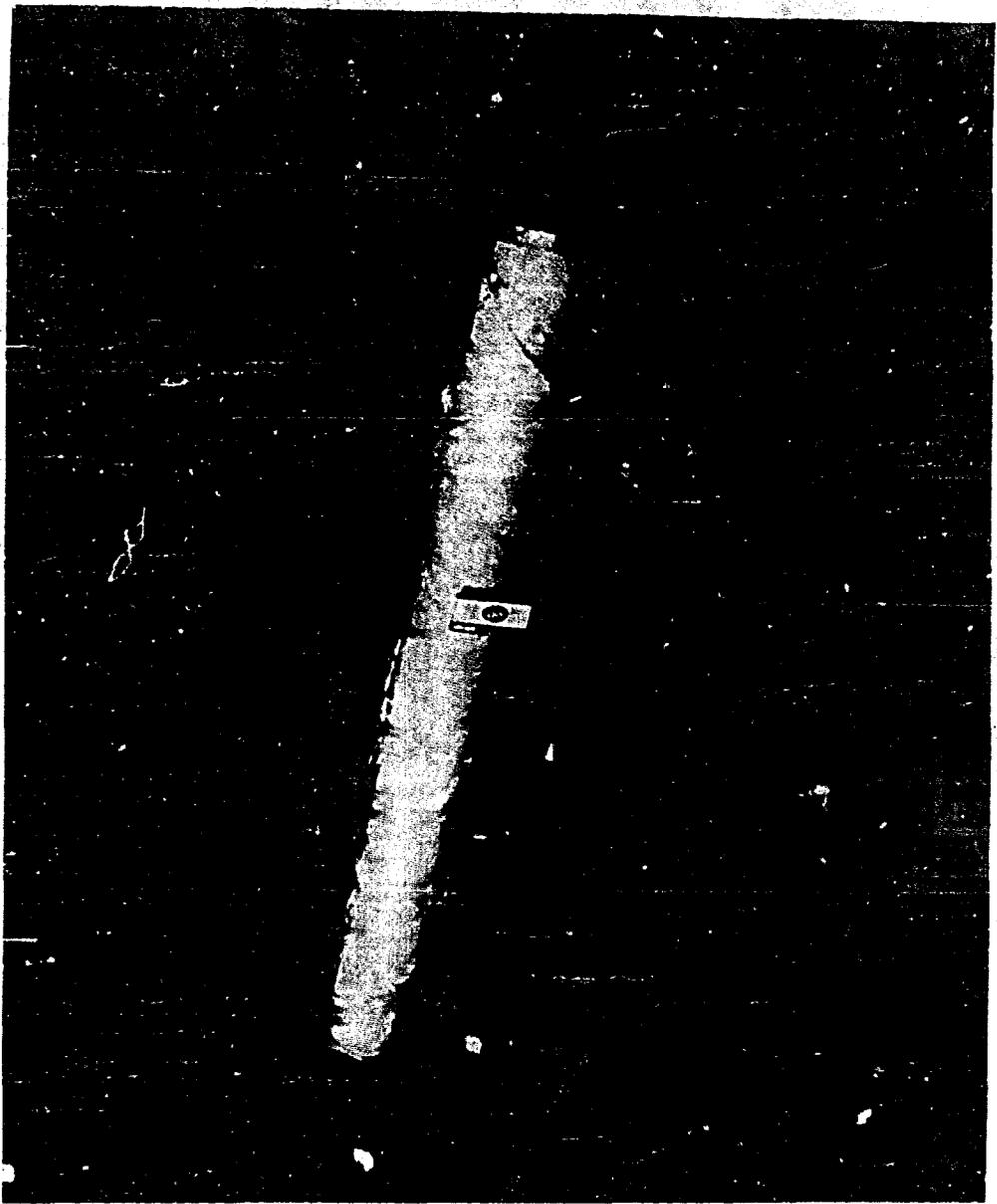
FIGURE 22. ROLLED UP 5 FT DIAMETER SOLAR COLLECTOR
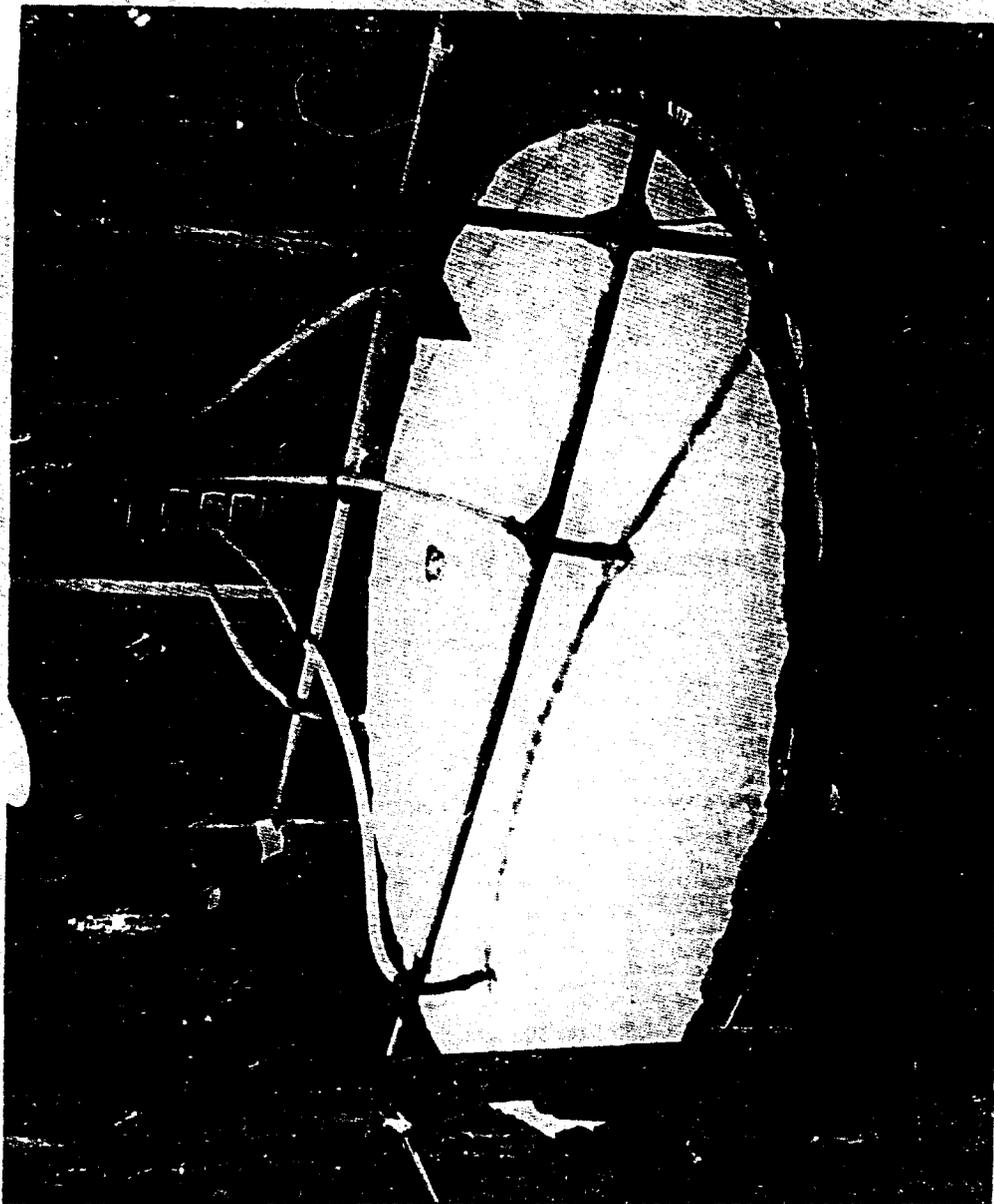
FIGURE 23. IMPREGNATED 5 FT DIAMETER SOLAR COLLECTOR IN VACUUM CHAMBER

-106-
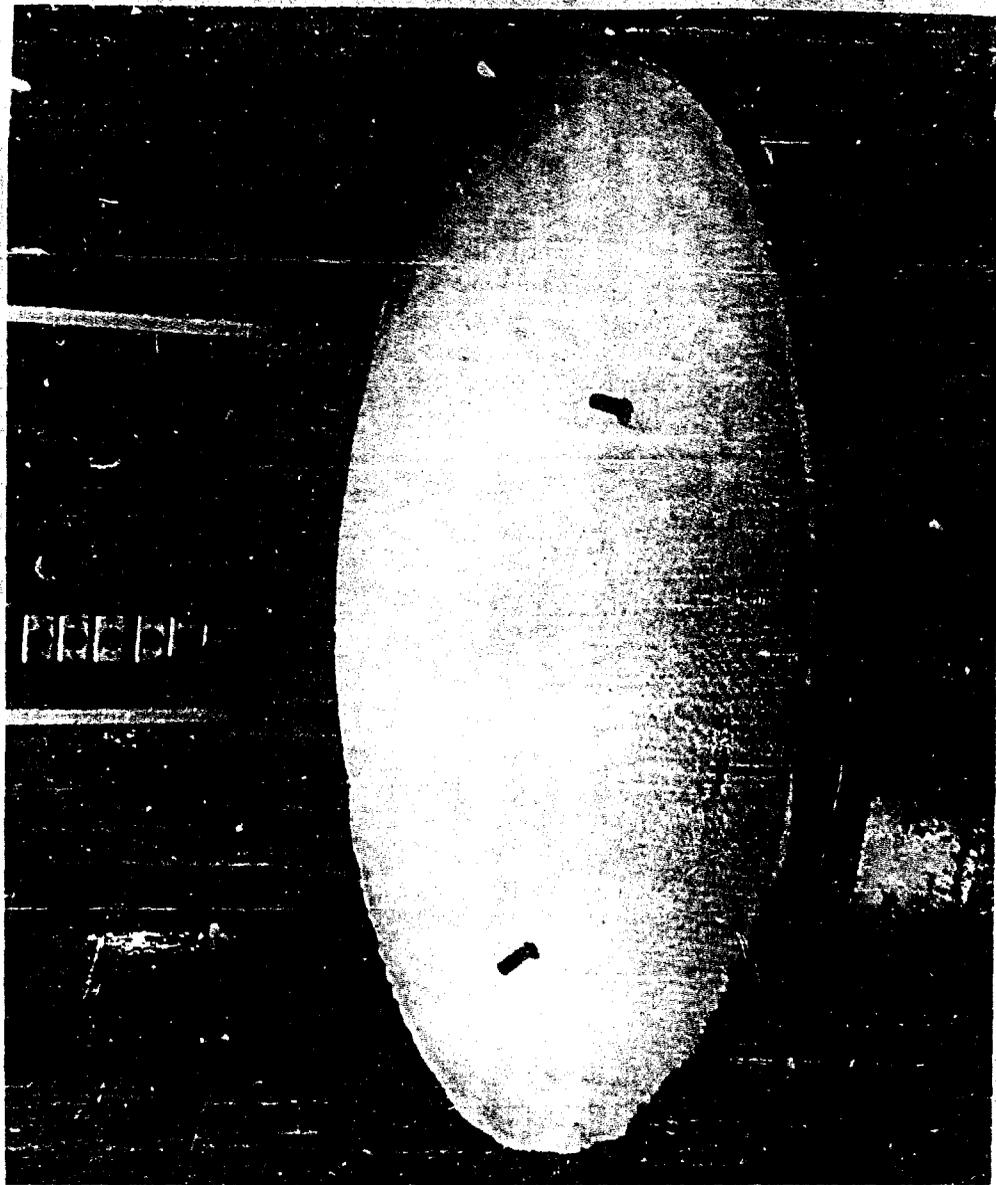
FIGURE 24. CURED STRUCTURAL MATERIAL ON 5 FT SOLAR COLLECTOR

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FIGURE 25. CURED 5 FT SOLAR COLLECTOR

FIGURE 26. CURED 5 FT SOLAR COLLECTOR